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Etna: a volcano in an identity crisis?

Boris Behncke, INGV-Osservatorio Etneo Catania, Italy

Mount Etna volcano in eastern Sicily is one of the most active volcanoes on Earth, and without any doubt the most versatile of all. Yet, most geology textbooks describe Etna as a predominantly effusive and essentially non-explosive basaltic volcano, a notion that is also profoundly anchored among the local population. For many centuries indeed, most eruptions produced voluminous lava flows, whereas explosive episodes were rare, although a few of the major flank eruptions in the 17th, 18th and 19th centuries showed significant explosive activity. Moreover, Etna is a volcano whose morphology changes in a manner and at a speed not seen at any other volcano on the planet. Since the late-1970s, episodes of explosive volcanism have become progressively more frequent and intense, mostly during summit eruptions, and since the late-1990s, such episodes have become the most characteristic eruptive manifestation at the volcano, with approximately 200 episodes of lava fountaining and copious tephra emission (so-called paroxysmal episodes). This change in the eruptive behavior forces the local population to deal with unprecedented challenges, such as handling large quantities of tephra fallout over population centers, lifelines and cultivated land. Closer to the mountain, popular hiking areas received exceptionally large clasts (scoriaceous bombs up to .5 m in diameter at 5-6 km distance from the summit), presenting an entirely new hazard at this volcano. The intense eruptive activity at Etna's summit in recent years has brought about impressive changes to the summit morphology, especially at the Southeast Crater, where since January 2011 a new cone (the New Southeast Crater) has grown, only to be overtopped in early 2017, by a new cone jokingly coined "The Very Very Newest Southeast Crater). Conspicuous changes occurred also in 2015-2016 at the other summit craters. Etna thus might seem a volcano in a sort of "identity crisis", but in reality, during its geological evolution, much larger explosive eruptions have occurred, such as, most recently, the 122 B.C.E. Plinian eruption.



Geophysical observations: the surficial signatures of volcanic activity

Gilda Currenti, INGV Catania, Italy

Etna volcano has becoming a reference natural laboratory for a multidisciplinary research programme that operates in a fruitful feedback mode between the advancement of monitoring techniques and the assessment of the geophysical observations by innovative modeling concepts. The multidisciplinary geophysical dataset gathered from ground-based and satellite monitoring networks during the last decades allows for investigating the behavior of the volcano in a period in which it exhibited different styles of activity characterized by inflation, flank eruptions and fountaining episodes. Integrated analysis and 3D numerical modeling of gravity, magnetic and deformation data are here presented for capturing the spatio-temporal evolution of the Etna volcano activity and, together with other volcanological evidences, for understanding the eruption mechanisms.



Plume and soil gas geochemistry: applications for volcano monitoring

Marco Liuzzo, INGV Palermo, Italy

Measuring the composition and the related quantity of gases released from active volcanoes provides important insight into our understanding of volcanic processes which, when combined with other methods, contributes significantly to volcano monitoring. Volcanic gases can now be measured using a large variety of highly sophisticated techniques, however, only a few of these are able to provide high-resolution routine measurements for permanent monitoring and, typically, for only a few compounds. An increased ability in monitoring volcanic activity through periodic measurements is also possible using several methods which make use of portable instruments. Here we review some of the techniques used in geochemical volcanic surveillance and expected results from methods applied in several case study examples from the INGV network of automatic monitoring stations installed on Etna and Stromboli and

other volcanoes worldwide. Attention will be specifically focused on plume geochemistry and volcanic soil degassing and related monitoring methods, including interpretative models of the expected behavior of degassing processes during and between eruptions. Examples of comparative multidisciplinary approaches, incorporating both volcanological and geophysical data will be presented within a coherent framework that further highlights how the geochemical data variations are closely related to observed volcanic activities. This overview of volcano geochemical monitoring techniques will demonstrate how the surveillance of active volcanoes using the featured methods may facilitate the forecasting of imminent eruptive activity and/or the tracking of the temporal evolution of an in-progress eruption thus playing an important contributory role in the planning of civil defense actions and significantly contributing to volcano hazard mitigation.

 **Anatomy of an unstable volcano: multiple processes affecting flank instability at Mt. Etna (Italy)**

Marco Neri, *INGV Catania, Italy*

Volcano deformation may occur under different conditions and processes. To understand how a volcano deforms, as well as relations with magmatic activity, we study in detail Mt. Etna using InSAR data, from 1994 to 2008, and geostructural field evidences. From 1994 to 2000, the volcano inflates with a linear behaviour. The inflation is accompanied by eastward and westward slip on the E and W flanks, respectively. The portions proximal to the Etna summit show higher inflation rates, whereas the distal portions show several sectors bounded by active faults, in some cases behaving as rigid blocks. From 2000 to 2003, the deformation becomes non-linear, especially on the proximal E and W flanks, showing marked eastward and westward displacements, respectively. This behavior results from the deformation induced by the emplacement of feeder dikes during the 2001 and 2002-2003 eruptions. From 2003 to 2008, the deformation approaches linearity again, even though the overall pattern continues to be influenced by the emplacement of the dikes from 2001 to 2002. The eastward velocity on the E flank shows a marked asymmetry between the faster sectors to the N and those, largely inactive, to the S. In addition, from 1994 to 2008 part of the volcano periphery (S, W and N lower slopes) experienced a consistent trend of uplift, on the order of 0.5 cm/yr. This data reveals that the flanks of Etna have undergone a complex instability resulting from three main processes. In the long-term (10^3 - 10^4 years), the load of the volcano is responsible for the development of a peripheral bulge. In the intermediate-term ($<10^1$ years, observed from 1994 to 2000), inflation due to the accumulation of magma induces a moderate and linear uplift and outward slip of the flanks. On the short-term (<1 year, observed from 2001 to 2002), the emplacement of feeder dikes along the NE and S rifts results in a non-linear, focused and asymmetric deformation on the E and W flanks. Deformation due to flank instability is widespread at Mt. Etna, regardless of volcanic activity, and remains by far the predominant type of deformation on the volcano.

 **Geochemical tracers as tools for volcanological research and monitoring**

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The study of magmatic fluids is based on the measurement and interpretation of concentrations, fluxes, and isotope ratios of the major gaseous species (H_2O , CO_2 , SO_2 , H_2S , HCl , N_2) and of a few key trace species such as noble gases (especially He, Ne, and Ar). These geochemical tracers are generally investigated in: 1) fluid and melt inclusions trapped in minerals and glasses during magma crystallization, at various stages of its ascent from the mantle toward the surface; 2) high- and lowtemperature fumarole and plume gases emitted from active craters; 3) thermal springs, soil emissions, etc., located along the flanks and peripheral zones of a volcanic system. Since the middle of the previous century, a number of geochemical studies revealed that the isotope ratios of carbon ($d^{13}C$ CO_2) and noble gases (mostly 3He / 4He) are among the most applied tracers to identify the relative contributions from different volatiles sources, which are intricately related to geodynamic setting (Ozima and Podosek, 2002; Hoefs, 2004; Dickin, 2005; Allègre, 2008; Burnard, 2012; Mason et al., 2017). $d^{13}C$ CO_2 has a long history of investigation (Naughton and Terada, 1954; Wasserburg et al., 1963; Allard et al., 1977) and is particularly useful to evaluate the extent of magmatic degassing (Marty and Jambon, 1987; Javoy et al., 1978;

Mattey, 1991; Trull et al., 1992; Shaw et al., 2004; Barry et al., 2014; Gennaro et al., 2017). In addition, it is often coupled to $^3\text{He}/^4\text{He}$ as $\text{CO}_2/{}^3\text{He}$ to distinguish proportions of carbon originating from magma, sediments and limestones (Sano and Marty, 1995), and evaluate the influx into the mantle wedge of CO_2 originated from subducting sediments (Gennaro et al., 2017; Mason et al., 2017). The study of $^3\text{He}/^4\text{He}$ in magmatic fluids further permits the definition of the magmatic/mantle source features, identify lower mantle contributions, contaminations at crustal levels and, when monitored over time, gives unambiguous signals of magma ascent in volcanic plumbing systems irrespective of the monitored magmatic system (e.g., Sano et al., 1995, 1997, 2015; Caracausi et al., 2003; Rizzo et al., 2006; 2009; 2015; 2016; Paonita et al., 2012; 2017). The information that arise from this variety of applications are fundamental for volcanological researches and represent the base for the following development of monitoring protocols.

PARTICIPANT ABSTRACTS



How diverse is microbial sulfate reduction? New Insights from the terrestrial and marine subsurface microbiomes

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Terrestrial and marine subsurface environments contain upwards of one fifth of all biomass, including microorganisms that drive organic carbon and inorganic compound transformations fundamental to the planet's biogeochemical cycles. In such anaerobic environments, >30% of all carbon turnover is conducted by sulfate reducing microbes that primarily utilize organic carbon as an electron donor in combination with sulfate as an electron acceptor. However, our knowledge of the microbial ecology of the terrestrial and marine subsurface ecosystems is extremely limited. In fact, the capacity to reduce sulfate to sulfide is only described in organisms from ten microbial lineages. Genome-resolved metagenomics, an approach that can yield near-complete and even finished genomes for organisms, has the potential to fundamentally transform our understanding of such ecosystems by enabling organism-resolved descriptions of elemental transformations and redox processes. From five distinct terrestrial and marine subsurface environments, we identified and investigated 123 near-complete genomes that contain dissimilatory sulfite reductases, thereby doubling the number of known lineages associated with sulfate reduction. Included amongst these are eight candidate phyla, and two of these lineages contain sequences that are inferred to be amongst the most ancient. Interestingly, we also identified ultrasmall putatively symbiotic CPR bacteria that contain a key sulfite reductase gene. We conclude that organisms from newly identified and little-studied lineages contribute significantly to sulfate reduction and the turnover of buried organic carbon in the subsurface.



Initial characterization of surface photosynthetic communities at the lagoa da furnas, Azores Islands

Armando Azua-Busto, Blue Marble Institute of Science, USA

The lagoa da furnas located in the Sao Miguel Island (one of the Azores Islands) is characterized by the presence of active fumaroles, solfatara and boiling water calderas. Interspersed on the surface of the high temperature soils we observed the up to date unreported presence of superficial patches of green color. A preliminary analysis showed that these were composed by a complex community of photosynthetic species, including colonial, unicellular and filamentous microalgae, cyanobacteria and other bacteria. The diversity of photosynthetic species was preliminary characterized by chlorophyll a autofluorescence and the internal ultrastructure of some of these species was characterized by transmission electron microscopy, showing that albeit the high temperature of this habitat, several photosynthetic species from two different domains of life have adapted to it.

**Biology Meets Subduction**

Peter Barry, Karen Lloyd, Katie Pratt, J Maarten de Moor, Donato Giovannelli, Taryn Lopez, and Daniel Hummer, University of Oxford, UK



Subduction is controlled by plate tectonics and represents the dynamic process of surficial/crustal material being transported into Earth's mantle over hundreds of millions of years. Biological processes control the overall composition of the material that is subducted, and thus biology and subduction processes are intimately related; however, for many researchers, disciplinary boundaries obscure this connection. Inspired by the multi-disciplinary DCO research, the Biology Meets Subduction project is an effort to understand the complex interplay between volcanic carbon and biology along the Costa Rican convergent margin. In February 2017, 25 scientists from 7 different countries conducted a field expedition with the goals of constraining the distribution of carbon between Earth's surface and deep reservoirs and understanding how it is controlled by the dynamic processes of subduction and volcanism. This project brought together the diverse expertise and methodology of scientists from all four of DCO's science communities at a single field focus site: the Costa Rica convergent margin. The team was composed entirely of early career scientists, conducting geochemical, biological, and petrological sampling, a task rarely if ever attempted in a single, coordinated campaign. In addition to the logistical novelty of this campaign, no one has conducted a comprehensive study separating the sources and pathways of biotic vs. abiotic C through a subduction zone. The primary scientific questions we are addressing are: (1) What is the influence of biological activity on C ingassing and outgassing at the Costa Rica convergent margin? (2) Can biological signatures be traced through subduction processes and distinguished from shallow biological cycling using isotopic constraints on subducted inputs and volcanic/forearc outputs? Using this information, can we (3) better constrain C sources and fluxes, and (4) improve deep C budget estimates for the Costa Rica convergent margin? The initial data is now being collected and the team is in the process of synthesizing the results in order to better understand the complex interplay between biology and geology on Earth.

**Impact of crustal differentiation on geological carbon cycle**

Omar Bartoli, Bernardo Cesare, Stefano Poli, *Padova University, Italy*

The modeling of the long-term C cycle is based on a subcrustal dynamic in which C input to the Earth's interior is controlled by subduction of C-bearing lithologies into the deep mantle, whereas volcanic processes liberate C from the interior to the exosphere. However, the modeling on the long-term C cycle largely overlooks potential contributions. In collisional settings where deep mantle magmas are forced to interact with the crust, often triggering the partial melting of crustal rocks, an additional important source of C for magmas is likely to be the buried organic material transformed to graphite during crustal metamorphism. Because graphitic crustal rocks are very common throughout the world and because these rocks cover the entire time from the formation of the early crust to the present, melting of graphitic rocks and subsequent ascent of large amounts of C-bearing crustal magmas might have represented an important contribution to deep C degassing. Our research aims to obtain the original C content of natural crustal magmas. To pursue this goal of paramount importance, we are studying small (<20 μm) inclusions of crustal melts – nanogranitoids– trapped within peritectic minerals of rocks which represent the residuum left after magma extraction. Nanogranitoids can provide the original H₂O and CO₂ contents of magmas before they undergo volatile degassing during ascent. Nanogranitoids may contain graphite or may coexist with primary polycrystalline inclusions. Raman and FIB-SEM investigation of the latter reveals the presence of Mg-, Fe-bearing carbonates, graphite and CO₂. This finding indicates the coexistence of silicate and carbonatitic melts in the deep graphitic crust. Owing to the important multiple interconnections, an interdisciplinary group of researches with expertise on sediment geochemistry, graphite formation and its chemical behavior at high temperatures, and on mechanisms and rates of ascent of C-bearing magmas should be assembled to evaluate the impact of crustal melting on geological carbon cycle.

**Sulphur and methane clumped isotopes of arc volcanic gases to trace volatile cycling in subduction zones**

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Isotopic signatures of S and C in arc volcanic gases reflect the input of sediments and slab-derived material, but can also be affected by secondary processes, including degassing, redox reactions or biogeochemical processes. Release of methane can also be significant in arc settings, and could be traced down to serpentinization of the mantle wedge, thermochemical breakdown of organic matter or microbial production. We will present sulphur isotope and methane clumped isotope data from low-temperature ($\leq 100^\circ\text{C}$) gases collected along the Costa Rica segment of the Central America Subduction Zone during the DCO “Biology Meets Subduction” expedition. We aim to discriminate between the sources of volatiles and variability of emissions across the arc. Our methane isotopologue data will improve our understanding of the source(s) of methane in volcanic gasses associated with subduction environments, and of potential microbiological adaptations to the conditions these environments often harbour. This will also inform our interpretation of the S isotopic compositions of the gases, which at low temperature may have suffered several processes before reaching the surface, potentially affected by redox-associated fractionation, disproportionation, scrubbing by the crustal medium, or S-utilizing deep biosphere. This type of analysis is also relevant for Sicilian volcanism, where methane-rich outgassing is manifested in the form of several mud volcanoes, and high CO_2 and S emissions point to an important sedimentary input, with a high contribution from a subducting carbonate component reflected by relatively high CO_2/ST ratios. Hence Etna is an ideal location to apply our tools to investigate the cycling of S, C and CH_4 in convergent settings.

**Cerium stable isotopes as a redox tracer in Early Earth environments**

Nina Bellot, Debaille V., Hofmann A., *Université Libre de Bruxelles, Belgium*



The long term carbon cycle on Earth is intimately related to the rise of O_2 in the atmosphere during the Great Oxidation Event (GOE) and the appearance and evolution of life over geological times. Studying the ocean and atmosphere redox conditions will bring additional information regarding the Earth carbon cycle. This work focuses on Cerium (Ce) element, more particularly on its behavior in different redox environments. Cerium (Ce) isotopes have the potential to give new clues regarding the redox state of sedimentary environments (Nakada et al., 2016). Cerium is a unique rare earth element (REE) as it forms tetravalent cations (Ce^{4+}) in oxidative environments, in contrast to other REEs that occur in the trivalent state ($3+$). Chemical sediments deposited in different redox environments may thus show Ce depletion or enrichment relative to neighbouring REE. The aim of this study will be to measure $^{136}\text{Ce}/^{142}\text{Ce}$ isotopes in samples from sedimentary successions deposited between 3.4 to 2.2 Ga in order to investigate potential isotopic fractionations linked to changes in redox conditions on the Earth’s surface. In order to do so, the following sedimentary samples will be studied: (1) Different facies of Palaeoarchean chert from the 3.4 Ga Buck Reef Chert, Barberton greenstone belt, obtained from the BARB-3 drill core. Chert facies reflect variations in physico-chemical conditions in the shallow marine environment of their formation; (2) Mesoarchean carbonate samples from the Chobeni Formation (Nsuzze Group, Pongola Supergroup). The carbonates formed in sub- to supratidal environments and contain a diverse assemblage of microbialites (Siahi et al., 2016); (3) Paleoproterozoic carbonates from drill core of the Francevillian Group of Gabon deposited 2.2 Ga ago. The carbonates were deposited after the Great Oxidation Event during the waning stage of the Lomagundi C isotope excursion in a shallow-water intracontinental setting (Préat et al., 2011). Despite the great geochemical potential of Ce isotopes, they still poorly studied mainly because of chemical and analytical difficulties. Improvements in mass spectroscopy instruments over the last years allows to measure them with great precision. Ce has four isotopes with contrasting abundances: $^{136}\text{Ce}=0.186\%$; $^{138}\text{Ce}=0.251\%$; $^{140}\text{Ce}=88.8\%$; $^{142}\text{Ce}=11.114\%$. The ^{138}Ce is the daughter isotope from ^{138}La disintegration with a half-life of $T_{1/2}=292.5\text{Ga}$. All three others are stable isotopes and we will be focusing on the $^{136}\text{Ce}/^{142}\text{Ce}$ ratio here. The idea would be to present by poster, the Ce chemical separation steps and the mass spectroscopy technics necessary in order to obtain great Ce stable isotope ratios. One chemical protocol have been developed in Clermont-ferrand (Laboratoire Magmas et

Volcans; Bellot et al., 2015) and a second one, based on Tazoe et al., 2007 and Nakada, et al 2016, is currently applied in Brussels (G-Time Laboratory). So at least two technics can be done to greatly separate Ce. Then the isotopic measurements are done on a NU-II MC-ICPMS in Brussel. The technical information about the NU mass spectrometer and how to analyse the Ce will also be presented on the poster in order to explain how it works and how Ce isotopes ratios are obtained. This work about Ce stable isotopes in sedimentary environments can bring additional information about the redox state of carbonated sediments deposited in different geological setting and times. Furthermore, Ce isotopes is a new powerful geochemical tool as a redox tracer and many diverse applications can be considered and discussed in the field of deep carbon cycle and life appearance.

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Stability of Carbonates at lower mantle conditions – a possible candidate for Carbon storage in the Earth's deep interior



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Carbonates are key phases in the chemistry and dynamics of our planet. They are present from marine environments down to the lower mantle and are directly connected to the CO₂ budget of our atmosphere. Their high pressure behavior is an important issue for the global dynamic processes, mantle metasomatism, diamond formation and the deep carbon cycle. In addition, carbonate-related element transport processes to the deep regions of the Earth and back are still not well understood. Evidences for the presence of carbonates in the mantle were given by the analysis of inclusions in natural diamonds originating from a depth more than 580 km: walstromite-structured CaSiO₃ was found to be included together with calcite and olivine and syngenetic inclusions host the assemblage walstromite-structured CaSiO₃ with CaTiO₃-perovskite [1]. These two findings (and others, e.g. [2]) provide insights, at least on a local scale, on the conditions and compositions of the mantle. Recently, there have been several studies enhancing the knowledge on the stability and properties of carbonates at high pressure and high temperature [3–8]. These studies further exhibited the occurrence of pressure-induced structural changes of carbonates at extreme pressures (e.g. strontianite [8], or rhodochrosite [5]). These structural changes might allow the formation of solid solutions between end members at mantle conditions that are immiscible at ambient conditions. Very important are the findings that magnesite can be stable along the geotherm down to the lower mantle. Spivak et al. [3] characterized magnesite, siderite and ferromagnesite at pressures up to 40 GPa and found a dependence of the spin transition for Fe on the composition of the solid solutions. The spin transition in siderite was also characterized by Cerantola et al. [4] and Müller et al. [7]. New data have been obtained, not only increasing our understanding of the stability and electronic configuration, but also for the elastic properties of carbonates in the aragonite structure [9]. At very high pressures, carbonates have been found to adopt complex structures containing rings of carbonate tetrahedra [10]. Those studies demonstrate that carbonates may be stable in the mantle and are potentially reaction partners for silicates throughout the Earth's mantle. However, the stability of carbonates in co-existence with mantle silicates remains unknown, so far. Based on thermodynamic calculations, Oganov et al. [10] predicted that carbonate breaks down in the presence of SiO₂ in basaltic environments. Experimental evidence for this prediction is still missing and we want to investigate this missing link between the stability of carbonates at mantle conditions on the one hand and the stabilities of carbonates in the presence of mantle silicates. We particularly focus on trace-element fractionation processes between carbonates and mantle silicates at relevant P,T-conditions using laser-heated diamond anvil cells. Sr and REE were found to be important trace elements in natural diamond inclusions formed at lower mantle conditions [1]. Therefore, first in-situ experiments were performed using synchrotron-radiation-based X-ray diffraction (XRD) and X-ray fluorescence (XRF) on Sr- and REE-doped

CaCO₃ together with mantle silicates (olivine, enstatite, wadsleyite and perovskite). To record the structural changes during reaction, we measured XRD maps over the heated area before and after heating and single-spots during heating. Our data shows a transformation of the starting silicates into bridgmanite (+ MgO in case of olivine and wadsleyite starting materials). In combination with spatially resolved XRF measurements over the same area, we observed changes in the elemental distribution of Sr, REE and Fe after heating. Additional optical fluorescence measurements and Transmission electron microscopy (TEM) analyses on the recovered sample material allowed us to document decomposition of the carbonates and enrichment of Sr and Eu among the newly formed perovskite phase. We can conclude that redistribution of the trace elements has occurred upon breakdown of the carbonates and that silicates may take up the trace elements that are provided by the carbonates. However, the conditions for carbonate stability in equilibrium with silicate phases at mantle conditions is not yet clear and has to be investigated in further experiments.

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Continental controls on a growing marine subsurface biosphere through recent geologic history

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We modeled the abundance of prokaryotes in subsurface marine sediments from modern Earth back to 140 Ma ago. The estimated cellular abundance, as determined was only about 40% at 140 million years ago versus contemporary earth. The concomitant migration of continents and accelerated sedimentation rates since the middle Cretaceous have led to the increase in cellular abundance. Independent lines of research corroborate enhanced weathering over this period (e.g. titanium and P/Fe ratios). The enhanced weathering and resulting increase in biomass has caused an increase of about 0.2 Pg P in the marine subsurface, entrained in biomass, which is 33% of the modern phosphorus reservoir in the surface ocean.

 **The role of C-O-H-S fluids in during the partial melting of eclogite in the cratonic mantle**

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Mantle metasomatism by C-O-H-S fluids has resulted in isotopic heterogeneities and the addition of new minerals such as diamond since the Archean [1]. While there is much interest on the influence of C-bearing fluids on the lithospheric mantle, the activity of S-bearing fluids and their role in diamond formation is less well constrained. Here we present a case study of eclogite metasomatism by S+C-rich fluids in the Kaapvaal craton mantle lithosphere. We combine experimental work and the analysis of sulphide-bearing eclogite xenoliths from key kimberlite occurrences in South Africa. The complementary investigations delineate the effect of S on the melting behaviour of eclogite, the relationship between volatile-bearing solidii in the upper mantle, the partitioning nature of various major and trace elements between the silicate residuum, sulphide residuum, and miscible or immiscible silicate+carbonate melts and sulphide melts. Comparison of the chemical signatures of minerals produced in the experiments with those in natural samples are a benchmark for the processes of volatile-bearing metasomatism that may be linked to diamond formation. [1] Griffin et al. (2003). *PrecRes* 127. 19–41.

 **Carbon storage within the Earth: is the amphibole an important reservoir at lower crust depths?**

Enrico Cannò, Tiejolo M., Moroni M., Ferrari E., Schiavi F., Dalla Ventura G., Giazzi G., Krotz L., *University of Milan, Italy*



Carbon (C) cycle and C fluxes between the mantle and the exosphere are critical processes for the Earth's atmosphere and climate on short to long time scales [1]. Recent estimates of C fluxes suggest that most of the subducted carbon is recycled through subduction processes, even if there is an apparent imbalance between the amount of C released from the subducting oceanic lithosphere and the amount that is returned to the atmosphere at volcanic arcs [2]. Current knowledge on C solubility in volatile-free major mantle minerals suggests their minor role in fixing C especially at low pressure [3]. Notwithstanding, no specific studied has been never carried out on amphibole that, although an accessory mineral of the upper mantle, is an important repository for volatiles. Amphibole crystal from crustal amphibole-rich peridotite from the Finero Complex (Ivrea Verbano; Italy) were considered and carbon was measured for different mineral fraction (63, 125 and 250 μm) with OEA. Data corrected for blank contamination suggest several hundreds of ppm of C in the analyzed amphiboles. Remarkably bulk rocks data reveal significantly lower C contents than amphibole separates. The presence of carbon was also investigated by spectroscopic methods (Raman and FT-IR). Our preliminary data suggest that investigated amphiboles have significant carbon contents but its structural position and speciation are still not clear. Additional determinations including $\delta^{13}\text{C}$ are in progress in order to better constrain the nature of the analyzed carbon.

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 **The transition from carbonatitic to carbonate-silicate magmas in carbonated eclogites**

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In the last decades, several studies focused on the effect of CO_2 on phase equilibria within carbonated eclogitic rocks to achieve information about the deep carbon cycle and the processes that control the carbon storage into the Earth's mantle. Nowadays the effect of temperature (T), pressure (P) and oxygen fugacity ($f\text{O}_2$) on the melt composition remains still unclear. This experimental study aims to determine the melt composition of CO_2 -rich melts at $f\text{O}_2$ buffered by the coexistence of carbon and carbonate as function of P and T. We performed experiments using Voggenreiter 840 t Walker-type multi anvil press available at HP/HT Lab at National Institute of Geophysics and Volcanology (INGV) in Rome. We employed for all the experiments a synthetic starting material representative of the Dolomite-Coesite-Diopside-Graphite buffering assemblage (DCDG; Luth, 1993), doped with FeTiO_3 and TiO_2 and ~3 wt% iridium used as redox sensor to calculate the oxygen fugacity during each experiment. The obtained results have been combined with published data (Stagno et al., 2015), and compared with thermodynamic

calculations (Luth, 1993). Preliminary results demonstrated that the transition from a carbonatitic melt (1-5 wt% SiO₂) formed at 900°C and a hybrid carbonate-silicate melts (20-25 wt% SiO₂) formed at 1200°C can occur within less than 1 log unit of fO₂ by a process called redox melting of elemental carbon-bearing eclogite rocks. Luth, R. W. (1993), *Science-New York then Washington*, 261, 66-66. Stagno, V., et al. (2015), *Contributions to Mineralogy and Petrology*, 169, 1-18.



Iron bearing carbonates stability in deep Earth interiors

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In the last century, the fast increase of CO₂ amount in the atmosphere together with the observed and correlated climate change have increasingly focused scientists' attention on the carbon cycle and its evolution at the Earth's surface. The carbon cycle, however, extends its roots well below the surface, where recent estimations locate up to the 90 % of the Earth's carbon budget, shared between the Earth's mantle and core. Due to the dynamic nature of processes characterizing our planet's interior such as upwelling and downwelling of materials via convection and subduction, there is a constant and more or less efficient recycle of carbon between the Earth's surface and its deep interior. Subduction is so far this study we focus our attention on carbonate phases, which are the main carbon-bearing minerals in subducting slabs, and in particular on the stability of Fe-carbonates such as siderite (FeCO₃). Indeed, previous experimental investigation on MgCO₃ has revealed its stability at pressures (P) and temperatures (T) down to the CMB. Due to the extensive solid solutions formed between MgCO₃ and FeCO₃ at ambient conditions, and the spin transition of Fe atoms at high pressures, which might influence the stability of the phase itself, we perform high pressures high temperatures experiments on FeCO₃ in order to study its stability and eventually determine its decomposition and transformation products at the relative P and T conditions. Experiments were performed using synthetic FeCO₃ crystals, at P and T over 110 GPa and 2500 K respectively. High pressures (HP) and high temperatures (HT) were achieved by mean of diamond anvil cells (DACs) and by double side laser heating. Neon was employed as pressure medium in DACs in order to preserve the single crystals status of the sample even after short laser heating period, from few minutes to above an hour long. X-Ray Single Crystal Diffraction (XRSD) and Synchrotron Mössbauer Source (SMS) experiments have been performed at ESRF and APS synchrotron facilities. Our results show that upon heating of FeCO₃ to Earth geotherm temperatures at pressures up to about 50 GPa, siderite partially dissociate forming different iron oxides. In particular, we show that below and above ~30 GPa the dissociation leads to the formation of α-Fe₂O₃ and h-Fe₃O₄ respectively. As reported by previous authors hematite and h-magnetite form as a result of partial redox dissociation of liquid-FeCO₃ leading to dissolved Fe³⁺ and CO₂ in the carbonate melt. At pressures above ~75 GPa we synthesised and solved the structures of two new compounds – tetrairon (III) orthocarbonate, Fe₄³⁺C₃O₁₂, and diiron (II) diiron (III) tetracarbonate, Fe₂²⁺Fe₂³⁺C₄O₁₃. Both materials contains CO₄ tetrahedra, and in particular the first of them is characterized by a unique structure, thus indicating that high pressure carbonates may be not similar to any other (including silicates) compounds. Based on a number of different dataset we infer that the orthocarbonate, Fe₄C₃O₁₂, forms directly from heating of FeCO₃ at T > 1400 K following the reaction $4FeCO_3 \rightarrow Fe_4C_3O_{12} + C$. The tetracarbonate, Fe₄C₄O₁₃, appears upon prolonged heating of Fe₄C₃O₁₂ above ~75 GPa but at temperatures significantly higher than those needed for the synthesis of the orthocarbonate following the possible reaction $8Fe_4C_3O_{12} \rightarrow 6Fe_4C_4O_{13} + 4Fe_2O_3 + 3O_2$. This means reduction of iron by oxygen, which has been already observed in studies of iron(III) oxide at pressure above ~70 GPa. Thus, we can conclude that tetracarbonate is the product of chemical evolution of the orthocarbonate. Moreover, Fe₄C₄O₁₃ was found to survive along entire geotherm to the depth corresponding to at least 2500 km demonstrating that self-oxidation-reduction reactions do not lead to destruction of carbonates in the Earth's lower mantle.

Fluid pathways in the mantle wedge : Influence of mineral grain size and mantle compaction

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Arc magmas are thought to be generated largely by hydrous melting induced by the addition of water from the subducting slab into the hot region of the overlying mantle wedge. While the release of fluids is predicted to occur over a wide region, arc volcanoes tend to form in a narrow region situated $\sim 100 \pm 30$ km above the top of the slab. To reconcile the availability of fluids in the wide region and the narrow surface distribution of arc volcanoes, there needs a mechanism that focuses fluids in the sub-arc region. The grain size distribution in the mantle wedge predicted by laboratory-derived laws was found to be a possible mechanism to focus of fluids beneath the arc region because of its control on the permeability of the mantle [Wada and Behn, 2015]. The viscous resistance of the mantle matrix to the volumetric strain, which generates compaction pressure and affects fluid flow, can also focus fluids towards the arc [Wilson et al, 2014]. We thus have developed a 2-D Darcy-Stokes flow model for the mantle wedge that combines both effects. We find that under the influence of both spatial variations in grain size and mantle shear viscosity, fluids tend to be focused beneath the arc for a range of subduction parameters. Further, we analyze the influence of fluid viscosity on fluid migration and provide a range of possible fluid pathways through the mantle wedge. Progressing our understanding of fluid migration paths from the slab to the overlying crust will provide insight into the recycling of volatile at subduction zones..

**HP-HT transformations of polycyclic aromatic hydrocarbons: phase transitions, oligomerization, decomposition, compressibility and thermal expansion.**

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Pressure and temperature effect on the behavior of polycyclic aromatic hydrocarbons (PAHs) has been intensively studied during recent years due to of their great importance in fundamental applied chemistry, Earth science and meteoritics. We studied transformations (oligomerization, polymerization and graphite/diamond formation) and thermal expansion of PAHs at 0-16 GPa and 300-1200 K. High-pressure experiments were performed using a Kawai-type multi-anvil apparatus and DAC. Part of experiments were conducted using in situ X-ray synchrotron radiation. The experimental products were studied by matrix-assisted laser desorption/ionization (MALDI) and Raman spectroscopy. In the pressure range of 1.5–15.5 GPa decomposition of PAHs was detected at 773–973 K. PAH graphitization at high pressures and temperatures occurs as a result of sequential oligomerization and polymerization of the starting material, caused by overlapping of π -orbitals, a decrease of intermolecular distances, and finally the dehydrogenation and polycondensation of benzene rings. The thermal expansion coefficients for PAHs was found to be extremely low at 2.9-12.5 GPa and 373-773K ($\alpha \sim 4,1 \times 10^{-5}$ K⁻¹). Based on the our results and previous experimental studies at ambient and high pressure we have identified PT diagram of PAHs phase transitions, oligomerization and decomposition parameters to 16 GPa and 1000 K. Defined PAHs phase diagrams are extremely important for understanding the planet accretion by carbonaceous chondrites.

**Looking for Carbonates in the Deep Earth: An experimental approach at extreme conditions**

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What carbon forms does nature hide in the most inaccessible parts of the deep Earth? An experimental approach of this mystery could possibly reveal what is the fate of carbonate rocks after subduction of the oceanic crust. Using diamond anvil cells to generate pressures, laser heating systems to obtain high temperatures and the advanced technology provided by synchrotron facilities, we are able to study in situ the behavior of various carbonate minerals at conditions that simulate the Earth's mantle. We particularly focus our interest on transition metal carbonates (Fe,Mn,Co,Zn,Ni) CO₃ in order to study the crystal chemistry of the calcite-type carbonates by means of single crystal X-ray diffraction and Raman spectroscopy. Our results provide new insights to the recent discoveries of tetracarboxates, suggesting that they can exist in the Earth's mantle, despite the reducing conditions that predominate. Using our

knowledge of the carbonate's stability fields from the surface to the lower mantle, we further investigate the possibility to detect the amount of carbonates that are introduced into the Earth using geophysical methods. To do so, we determine the elastic wave velocities of realistic carbonate mineral compositions in the (Ca-Mg-Fe) CO₃ system by means of Nuclear Inelastic Scattering. Our results reflect the great anisotropic behavior of carbonates that could possibly explain the anisotropic anomalies observed in the transition zone depths and confirm the presence of carbonate reservoirs. New carbonate phases and their seismic signatures await to be discovered and thus experiments continue.



Methane Dynamics in a Tropical Serpentinizing Environment: The Santa Elena Ophiolite, Costa Rica

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Uplifted ultramafic rocks represent an important vector for the transfer of carbon and reducing power from the deep subsurface into the biosphere and potentially support microbial life through serpentinization. This process has a strong influence upon the production of hydrogen and methane, which can be subsequently consumed by microbial communities. The Santa Elena Ophiolite (SEO) on the northwestern Pacific coast of Costa Rica comprises ~250 km² of ultramafic rocks and mafic associations. The climatic conditions, consisting of strongly contrasting wet and dry seasons, make the SEO a unique hydrogeological setting, where water-rock reactions are enhanced by large storm events (up to 200 mm in a single storm). SEO's hyperalkaline springs have elevated methane concentrations, ranging from 145 to 900 μM, in comparison to the background concentrations (<0.3 μM). The presence and potential activity of microorganisms involved in methane cycling in serpentinization-influenced fluids from different sites within the SEO were investigated using molecular, geochemical, and modeling approaches. These results were combined to elucidate the bioenergetically favorable methane production and/or oxidation reactions in this tropical serpentinizing environment. The hyperalkaline springs at SEO contain a greater proportion of Archaea and methanogens than has been detected in any terrestrial serpentinizing system. Archaea involved in methanogenesis and anaerobic methane oxidation accounted from 40 to 90% of total archaeal sequences. Genes involved in methanogenic metabolisms were detected from the metagenome of one of the alkaline springs. Methanogenic activities are likely to be facilitated by the movement of nutrients, including dissolved inorganic carbon (DIC), from surface water and their infiltration into serpentinizing groundwater. These data provide new insight into methane cycle in tropical serpentinizing environments.

Processes controlling crystal exchange between different magmas

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Fluid interactions within magma chambers are lost in the final snapshot frozen in bedrock. Fortunately, crystals provide a clue into the intricate exchanges between melts. Inconsistencies in crystal compositions between crystal core and rim suggest crystals interacting with different magmas (e.g. Waight et al. (2000); Tepley and Davidson (2003)). The overarching models for these interactions are (1) two liquid magmas mixing and (2) liquid magma melting the crust. In order to better understand the crystal exchange process, we explore buoyancy driven magma convection with crystals moving freely through the domain. Our simulations solve the equations for conservation of mass and momentum. In the model, we explicitly solve the multi-phase system without any assumptions on how the liquid drives crystals and how crystals alter the pressure field. By avoiding flow assumptions, we are able to capture growth and suppression of instabilities. To address the two models above, we suggest that the crustal crystal and liquid interactions (Case 2) is a viscous end member case of the 2 liquid magmas mixing model (Case 1). The main factor that governs flow trajectories of each phase is the relative velocities of the phases. With this motivation, we initially compare the buoyancy instability due to two different magmas to the instability due to varying volume density of crystals. The instability of crystals dependent on crystal parameters such as density, volume density, and size. The second focus on understanding crystal exchange processes is crystal lubrication. Lubrication, which is dependent on viscosity, determines if the crystal flow instability grows or stabilizes. If the instability grows, crystals will interact with neighboring magma. If the instability stabilizes,

crystals will stay in the host magma. Crystal transportation will identify the secular changes in the crystal chemistry. Pisgah Crater (Mojave Desert, Mexico) (Ramos and Reid, 2005), Lachlan granites (southeast Australia) (Waight et al., 2000), Chaos Crags (Lassen Volcanic Center, CA, USA) (Wallace and Bergantz, 2005), Rum gabbros (northwest Scotland) (Tepley and Davidson, 2003), Shap Granite (northwest England) (Cox et al., 1996), and El Chichon volcano (Mexico) (Davidson et al., 2001) are different field sites that may be exemplary of the discussed processes.



Spatially Resolved SO₂ Flux From Mt Etna and Correlation between geochemical and geophysical data

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Mt. Etna volcano contributes time-averaged SO₂ flux emissions of 2 Mt/a corresponding to about 10-15% of global volcanogenic budgets. The studies of SO₂ flux bring important information on how active volcanoes work helping to understand the shallow magma dynamics thanks to the propriety of this gas of exolving at shallow depth, therefore give the possibility to use it as parameter for volcano monitoring. Over the last few years, the technical advances on remote sensing SO₂ flux measurements with UV imaging opened a new window on the continuous monitoring of the degassing activity and offered insights on the transition from quiescence to explosive eruptions and on the integration between geochemical and geophysical dataset. The UV Camera allows to measure SO₂ flux from volcanic gas, and to measure the gas velocity from the uv images, taking advantage on this UV camera is often use in combination with other instrument, Multigas, in order to know the gas flux from the measured gas ratio of the other gases with SO₂, and the Lidar, in order to know the gas velocity to calculate the CO₂ flux. We demonstrate that our vent-resolved SO₂ flux time series allow capturing shifts in activity from one vent to another and contribute to our understanding of Etna's shallow plumbing system structure. Two SO₂ cameras, installed at Pizzi Deneri and La Montagnola (2 km and 3.5 km from the craters), allowed to separately resolve degassing activity of individual summit craters of Etna (North East Crater, NEC, and New South East Crater, NSEC) with a high temporal (~1Hz) and spatial resolution (a few meters). Our high resolution geochemical dataset was compared with seismic and infrasonic dataset provided by the geophysical network run by the INGV of Catania. The 2014 Etna's Eruption data shows that both geophysical signals (tremor and infrasound) and SO₂ degassing shifted toward the NSEC shortly prior/during the eruption, pointing to a clear displacement of the magma/gas mixture within the active craters. The simultaneous variation of SO₂ flux within the summit craters would demonstrate some level of interconnectivity between the craters (which SO₂ flux time-series are inversely correlated) in the shallow conduit system. We demonstrate that our vent-resolved SO₂ flux time series, of 2014 Etna Eruption, allow capturing shifts in activity from one vent to another and contribute to our understanding of Etna's shallow plumbing system structure. We find that the fissure eruption contributed ~50,000 t of SO₂ or ~30% of the SO₂ emitted by the volcano during the 5 July to 10 August eruptive interval. Activity from this eruptive vent gradually vanished on 10 August, marking a switch of degassing toward the NSEC. Onset of degassing at the NSEC was a precursory to explosive paroxysmal activity on 11-15 August.



Magmatic Outgassing into the Earth's Early Atmosphere

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The outgassing of volatile compounds of C-O-H-S from magmatic melts represents an important input into the Earth's atmosphere over the course of its evolution. The volatile inventories in these melts are dependent on temperature, pressure and oxygen fugacity. In addition, the melt concentrations of volatiles themselves affect the redox balance and resulting oxidation state of the melt. This, in turn, influences the relative solubilities of these compounds and the concentrations of volatile species outgassed into the atmosphere. On the early Earth, volatiles in the magmatic reservoir were an important driver of atmospheric composition, and may have played a role in the build up of oxygen that led to the Great Oxygenation Event. We present preliminary results of a volcanic outgassing model for the early Earth, which includes redox reactions between volatile species and iron in the melt reservoir. With particular

attention to carbon and sulfur inventories, we simulate the relative concentrations of reduced (CO , CH_4 , H_2S , H_2) and oxidized (CO_2 , SO_2 , H_2O) species from magmatic melts into the atmosphere. We further explore the effect of mafic versus felsic melt compositions on the outgassed species, and their potential influence on Earth's atmosphere over time.



Pre-eruptive volatile contents of silicate melt in active volcanic systems: a melt inclusion perspective

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The physical and chemical properties of magmas, and the dynamics of volcanic eruptions, are largely controlled by the volatile (H_2O , CO_2 , S, Cl, F) budget of the melt. Partitioning of volatiles between melt and magmatic vapor significantly impacts global climate and ore-forming processes, and heat advection around volcanic edifices is sensitive to the type of fluid exsolving from magmas. In addition, the type of magmatic vapor exsolving from melts in sub-volcanic environment also affects the explosivity of volcanic eruptions. Volatile contents of the glass in silicate melt inclusions (MI) provide indirect information on the compositions of exsolved vapors, via solubility and partitioning modeling. Indeed, MI provide the only method available to measure directly the pre-eruptive volatile contents of deep, undegassed melts, which is a key parameter to understanding the compositions of exsolved fluids. My research focuses on the behavior of volatiles in silicate melt systems. In particular, I study how volatiles in silicate magmas associated with active volcanoes influence the volcanological processes by employing the fluid-melt inclusion technique. My expertise is in the use of this technique as a tool to better understand the role of volatiles in undegassed/partially-degassed magmas. On one hand, my research has focused on estimating the crustal depths, dynamics of magma reservoirs, and pre-eruptive volatile contents beneath active volcanic systems (e.g., Mt. Somma-Vesuvius, Italy) using MI. On the other hand, it has focused on how reliably a scientist can use MI to understand the volatile content of deep magmas.



Exploring the influence of the liquid-liquid phase transition of water on geochemical processes

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Pure water and aqueous fluids undergo a structural transformation during compression from a low-density form (LDW) to a high-density form (HDW). Given the ubiquity of hydrous fluids in Earth and planetary interiors and their unique role in geochemical and biological processes, the possible influence of such a structural phase transition on geochemical processes shall be addressed. We particularly investigate the high-pressure behaviour of pure water and carbonate and bicarbonate-bearing fluids by in situ Raman spectroscopy, through the LDW-HDW transition with an unprecedented spectral and pressure resolution. Our results show that the compression of liquid water induces a progressive transfer of water molecules from the intermediate water population mostly to the network water populations, broken by a steady distribution across the LDW-HDW transition. Adding solutes such as Na_2CO_3 and NaHCO_3 stabilizes the structure of the low-density form of water, enlarging its stability domain and deferring the occurrence of the LDW-HDW transition of water towards higher pressures. Increasing the Na_2CO_3 concentration to 2 m leads to a structural ordering of water molecules towards a stable and fully bonded water network constituted of relaxed H bonds, likely due to the strong kosmotropic character of carbonate ions. Our results also show that the aqueous ions are less compressible in the high-density regime and that the compressibility of bicarbonate ions is always twice larger than that of carbonate ions, whatever the form of water. The influence of the liquid-liquid phase transition of water on the dissolution of sulfate minerals at high pressure will also be discussed.



What is the CO_2 budget of basaltic magmas?

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Volcanoes inject significant amounts of CO_2 into the atmosphere during active and passive degassing, contributing to the global C cycle. There are a variety of techniques to measure current CO_2 emissions (e.g., soil CO_2 flux, fumarole and plume sampling) but when compared to our best approximation of

undegassed magmas (melt inclusions) far more CO₂ is emitted than reconciled petrologically. This prevents us from obtaining accurate estimates of past volcanic CO₂ emissions. Melt inclusions are tiny pockets of melt trapped inside growing crystals. The crystal acts as a pressure vessel, preventing the inclusion from degassing. It is these melt inclusions that are a window into the magma during ascent to the surface. Unfortunately, CO₂ begins to exsolve at very high pressures, potentially before crystals grow, and high CO₂ melt inclusions are more likely to undergo decrepitation. This means the CO₂-content trapped in melt inclusions is a minimum estimate only. When magma ascends, volatiles trapped within the magma exsolve. During ascent, CO₂ isotopically fractionates whereby ¹³C preferentially enters the vapour phase, leaving behind ¹²C in the melt. This ¹²C-enriched melt can be recorded in melt inclusions allowing calculation of the initial CO₂ concentration of the melt, its initial isotopic signature, and the style of degassing that occurred even when high CO₂ melt inclusions are not trapped. This provides us with the first method for estimating the CO₂ budget of past eruptions.

 **Methane origin at the Ciomadul volcano: methane concentration above 1% in a volcanic area**

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The Ciomadul volcanic complex is the youngest volcano of the Carpathian-Pannonian area. A very intense degassing of carbon dioxide from mofettas, bubbling pools and diffuse emissions characterises the area. Until now, the hydrocarbon gases were not characterised from a geochemical point of view. Consequently, several sampling campaigns were undertaken in 2015 and 2016 to collect gas samples from the different gas manifestations of the area. Methane and other light hydrocarbons are usually found in ppm levels in volcanic regions; however, it was observed that methane concentration at Ciomadul ranges between 0.06 up and 2.38 vol.%. Based on the stable isotopic analyses of methane from the collected samples ($\delta^{13}\text{C}-\text{CH}_4$ and $\delta^2\text{H}-\text{CH}_4$ are in the range -28.3 to -7.8% VPDB and -144 to -124% VSMOW respectively), suggesting that methane is of thermogenic origin and a contribution of abiotic methane cannot be excluded. Similar values were also recorded in fumaroles from volcanic systems (e.g., of Panarea and Pantelleria); and in geothermal systems (e.g., Mt. Amiata, Larderello and Latera), suggesting an abiotic origin for methane discharged in volcanic systems. The processes attributed to the abiotic methane generation in these systems were CO₂ reduction and/or Fischer-Tropsch type reactions. The questions about the reason of such a high concentration of methane in this volcanic area, and what processes could generate it still persist. This research belongs to the scientific projects supported by the OTKA (Hungarian National Research Fund) project number K116528; the Romanian National Research Council, CNCS – UEFISCDI, project number PN-II-ID-PCE-2011-3-0537; European Union and the State of Hungary, co-financed by the European Regional Development Fund in the project of GINOP-2.3.2-15-2016-00009 ‘ICER’.

 **Using noble gas systematics to constrain fluxes of volatiles between terrestrial reservoirs**

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Noble (inert) gases (He, Ne, Ar, Kr and Xe), and their numerous isotopes, can be used as tracers of volatiles (including H₂O and C) in terrestrial systems. Measuring noble gases in igneous samples (e.g., volcanic scoria, mantle xenoliths, gas) enables us to accurately constrain the origin, preservation, and fluxes of volatiles between the Earth’s surface and mantle. New noble gas results are presented for a suite of samples from La Palma, one of the youngest manifestations of the Canary Island hotspot. A geothermal gas sample yielded the highest ³He/⁴He ratio reported thus far (12 Ra), suggesting the involvement of a primordial mantle reservoir in the source of these ocean islands. We combine these geochemical measurements with geodynamical modelling to investigate the evolution of mantle heterogeneity and the fluxing of volatiles over the course of Earth history. We utilise the geodynamical model of Brandenburg et al., 2008, which satisfies the geophysical constraints of oceanic heat flow and average plate velocities, as well as geochemical observations, such as the amount of ⁴⁰Ar in the atmosphere. This model also reproduces the geochemical distributions observed in multiple isotope systems (e.g., U-Th-Pb, Rb-Sr, Sm-Nd, Lu-Hf), which define mantle endmembers. The model has been

updated to produce higher resolution results and to include a self-consistent reorganisation of the plates to with regions of up-/down-wellings. The model is run for the full age of the Earth (4.5 Ga) and enables us to powerfully visualise the geochemical evolution of the Earth's mantle.

Melt focusing and CO₂ extraction at mid-ocean ridges: simulations of reactive two-phase flow

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The deep CO₂ cycle is the result of fluxes between near-surface and mantle reservoirs. Outgassing from mid-ocean ridges is one of the primary fluxes of CO₂ from the asthenosphere into the ocean-atmosphere reservoir. Focusing of partial melt to the ridge axis crucially controls this flux. However, the role of volatiles, including CO₂ and H₂O, on melt transport processes beneath ridges remains poorly understood. We investigate this transport using numerical simulations of two-phase, multi-component magma/mantle dynamics. The phases are solid mantle and liquid magma; the components are dunite, MORB, hydrated MORB & carbonated MORB. These pseudo-components capture accepted features of mantle melting with volatiles. The fluid-dynamical model is McKenzie's formulation [1], while melting and reactive transport use the R_DMC method [2,3]. Our results indicate that volatiles cause channelized melt transport, which leads to significant fluctuations in volume and composition of melt focused to the axis. The volatile-induced expansion of the melting regime at depth, however, has no influence on melt focusing; distal volatile-rich melts are not focused to the axis. Up to 50% of these melts are instead emplaced along the oceanic LAB. There, crystallization of accumulated melt leads to enrichment of CO₂ in the deep lithosphere, which has implications for carbon recycling by subduction. Results from a suite of simulations, constrained by catalogued observational data [4,5,6], enable prediction of global MOR CO₂ output. By combining observational constraints with self-consistent numerical simulations we obtain a range of CO₂ output from the global ridge system of 53–110 Mt CO₂/yr, corresponding to mantle concentrations of 100–200 ppm CO₂.

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At the interface of geology and biology: Occurrence of methane down to 2.5 km depth within the Precambrian Fennoscandian Shield



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Methane is a common constituent in deep saline fluids in Precambrian continental shields. It is also an important electron donor in anoxic deep biosphere. In groundwaters within the Fennoscandian Shield in Finland CH₄ concentrations of up to tens of mM can be found. Compared to N₂ dominated groundwaters, CH₄ dominated groundwaters have higher gas/water ratios clearly indicative of accumulation of gas after groundwater recharge in the crust. However, taking into account the age (~1.9 Ga), high metamorphic grade, and organic carbon deprived nature of the bedrock the occurrence of such large amounts of CH₄ is enigmatic. In order to elucidate abiotic and biotic controls on hydrocarbon formation in deep (down to 2.5 km) continental bedrock groundwaters we examined the presence and isotopic composition of CH₄ and other hydrocarbons and related fluid and mineral phases at the Outokumpu Deep Drill Hole and the Pyhäsalmi Mine in Finland and compared the results with previous data from fifteen other sites across the central Fennoscandian Shield (Kietäväinen et al. 2017). Comparison of gases and regional lithology demonstrated that CH₄ is relatively abundant in metasedimentary regions. The rock types in these areas today comprise schists and gneisses. An especially large amount of CH₄ was found in areas consisting of organic carbon rich rock types, black schists. In these areas, up to 90% of the gas can be composed of hydrocarbons. In contrast, very little CH₄ is found from granitic and ancient volcanic regions. Thus, it

seems that even though purely abiotic mechanisms, such as natural analogues of Fischer-Tropsch type synthesis, can account for CH₄ production in the crust, organisms have an important and possibly unexcelled role in the process of carbon accumulation. Rather than a thermogenic relic the abundant crustal CH₄ within continental shields is more likely the result of long-term, but still on-going, low temperature formation from ancient organic compounds and their inorganic intermediates. Based on thermodynamic calculations, it can be predicted that methanogenesis from graphite and H₂ is a plausible mechanism of which also microorganisms may take advantage. However, especially below 1.5 km, CH₄ appears to be dominantly abiotic, which is evidenced, among other features, by its exceptionally heavy carbon isotope composition. Based on isotopic analysis of fracture calcites, indications of CH₄-oxidizing microbes could also be found near the active fracture zones in the upper 1 km of the bedrock. Reference: Kietäväinen R., Ahonen L., Niinikoski P., Nykänen H., Kukkonen I.T. (2017) Abiotic and biotic controls on methane formation down to 2.5 km depth within the Precambrian Fennoscandian Shield. *Geochim. Cosmochim. Acta* 202, 124-145.



Effect of pressure on the speciation of carbon in silicate melts and crystals at high pressure up to 8 GPa: Insights from multi-nuclear solid-state NMR



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The structural changes of carbon in crystalline and amorphous silicates at high pressure is essential to understand the geochemical evolution of the Earth's atmosphere, the composition of melts in mantle, and the overall distribution of carbon in the deep mantle. The structural changes around carbon in silicate melt under compression up to ~4 GPa have been extensively studied (e.g., Brooker et al., *Chem. Geol.*, 2001, 174, 225-239; Kohn et al., *Geochim. Cosmochim. Acta*, 1991, 55, 3879-3884; Morizet et al., *Geochim. Cosmochim. Acta*, 2014, 144, 202-216; Mysen, *Chem. Geol.*, 2013, 346, 113-124). However, the speciation of carbon in crystalline and amorphous silicates with varying pressure is not fully understood due to the lack of suitable experimental probes and the limitations on synthesizing the sample above 4 GPa using piston cylinder. Multi-anvil apparatus with an 18/11 assembly can achieve pressures of ~15 GPa, but the sample weight is limited to ~ 15 mg based on silicate melts while ~ 100 mg of a sample can be synthesized by piston cylinder with a 1/2" assembly. The recent breakthroughs in high-resolution solid-state nuclear magnetic resonance (NMR) allowed us to explore the detailed atomistic configuration in silicate melts and crystals with varying composition (e.g., Kim and Lee, *Geochim. Cosmochim. Acta*, 2013, 120, 39-64; Lee, *Solid State Nucl. Mag. Reson.*, 2010, 38, 45-57; Lee, *P. Natl. Acad. Sci. USA*, 2011, 108, 6847-6852; Lee et al., *J. Phys. Chem. C*, 2016, 120, 737-749). In this study, we explore the atomic configurations around the carbon species formed during the reaction between ¹³C-enriched amorphous carbon and MgSiO₃ enstatite synthesized at 1.5 GPa and 1400 °C using ¹³C magic angle spinning (MAS) NMR spectroscopy and Raman spectroscopy. We also provide the systematic protocols to characterize carbon-bearing fluid inclusions and other carbon-bearing species using high-resolution ¹³C solid-state NMR. Finally, we identify carbon species in binary sodium trisilicate melts (Na₂O-3SiO₂, NS3) and ternary sodium aluminosilicate melts (NaAlSi₃O₈, albite) at high pressure up to 8 GPa, which is much higher than previously studied, using solid-state ²⁷Al, ²⁹Si, and ¹³C MAS NMR spectroscopy. ¹³C MAS NMR results for carbon-bearing enstatite show that the sharp peak at 125.2 ppm is dominant. While the peak could be assigned to either molecular CO₂ in the fluid phase or fourfold-coordinated carbon ([4]C), the peak is likely due to fluid CO₂, on the basis of its narrow peak width with negligible spinning sideband intensity, insights from the quantum chemical calculations, and Raman analyses of micrometer-sized fluid inclusions in the sample. The peaks at 161.2, 170.9, and 173.3 ppm in the ¹³C NMR spectrum correspond to the carbonate ions (CO₃²⁻) and additional small peak at 184.5 ppm can be attributed to carbon monoxide. To evaluate whether the observed ¹³C NMR peaks stem from the structurally incorporated carbons in the enstatite or those in external phases, we established a calibration curve between ¹³C abundance and peak intensity in the ¹³C MAS NMR spectra using ADM-SiO₂ mixtures. Based on the established relationship, the estimated ¹³C amounts of CO₂, CO₃²⁻, and CO species are much larger than those estimated from carbon solubility in the crystals, indicating that those carbon species in enstatite-amorphous carbon reaction products are from external phases (Kim et al., *Am. Mineral.*, 2016, 101, 1113-

1124). ^{13}C MAS NMR spectra for carbon-bearing albite melts show multiple peaks of carbon environments, such as CO , CO_2 , and CO_3^{2-} , and there are at least four carbonate species, including $[\text{4}]\text{Si}(\text{CO}_3)[\text{4}]\text{Si}$, $[\text{4}]\text{Si}(\text{CO}_3)[\text{4}]\text{Al}$, $[\text{4}]\text{Al}(\text{CO}_3)[\text{4}]\text{Al}$, and free CO_3^{2-} . The fraction of $[\text{4}]\text{Si}(\text{CO}_3)[\text{4}]\text{Al}$ increases with increasing pressure, while those of other bridging carbonate species decrease, indicating that the addition of CO_2 may enhance mixing of Si and Al at high pressure. The ^{27}Al triple quantum (3Q) MAS NMR spectra for carbon-bearing albite melts revealed the pressure-induced increase in the topological disorder around $[\text{4}]\text{Al}$ without forming $[\text{5,6}]\text{Al}$. These structural changes are similar to those in volatile-free albite melts at high pressure, indicating that the addition of CO_2 in silicate melts may not induce an additional increase in the topological disorder around Al at high pressure. A noticeable change is not observed in ^{29}Si NMR spectra for the carbon-bearing albite glasses with varying pressure. These NMR results confirm that the densification mechanisms established for fluid-free, polymerized aluminosilicate melts can be applied to the carbon-bearing albite melts at high pressure (Kim et al., *Geochim. Cosmochim. Acta*, under review). The ^{29}Si MAS NMR spectra for partially depolymerized, carbon-bearing NS3 glasses show that the fraction of $[\text{5,6}]\text{Si}$ increases with increasing pressure at the expense of Q3 species ($[\text{4}]\text{Si}$ species with one non-bridging oxygen as the nearest neighbor). The pressure-induced increase in topological disorder around Si is evident from an increase in peak width of $[\text{4}]\text{Si}$ with pressure. ^{17}O NMR spectrum shows that the fraction of Na-O- $[\text{5}]\text{Si}$ in carbon-bearing NS3 melts is less than that of carbon-free NS3 melts at 6 GPa potentially due to the formation of bridging carbonate species. While its presence is not evident from the ^{17}O NMR spectrum primarily due to low carbon concentration, ^{13}C MAS NMR results imply the formation of bridging carbonates, $[\text{4}]\text{Si}(\text{CO}_3)[\text{4}]\text{Si}$, above 6 GPa. The formation of bridging carbonates can be used as a structural proxy for the increase in the polymerization of silicate melts at high pressure (Kim et al., *Geochim. Cosmochim. Acta*, under review). The ^{13}C MAS NMR spectra for carbon-bearing albite melts provide quantitative information about the speciation of carbon in the silicate melts at high pressure by measuring the peak intensity for carbon species and taking into consideration of the spin-lattice relaxation time (T_1). The T_1 relaxation time of CO_2 in albite melts increases with increasing pressure from 42 s (at 1.5 GPa) to 149 s (at 6 GPa). Taking the pressure-induced change in T_1 of carbon species into consideration, total carbon content in carbon-bearing albite melts increases with pressure from ~ 1 wt% at 1.5 GPa to ~ 4.1 wt% at 6 GPa. Furthermore, the calibrated fraction of CO_2 in albite melts matches well with the theoretical results of the fraction of CO_2 in rhyolite melts at 5 GPa. The results also reveal a noticeable drop in the peak intensity of free carbonates in carbon-bearing NS3 melts at 6 GPa, implying a potential non-linear change in the carbon solubility with pressure (Kim et al., *Geochim. Cosmochim. Acta*, under review). While direct probing of carbon species at concentrations below 5-10 ppm (e.g., carbon dissolved in the crystalline lattice) using NMR is challenging, the current results and method can be utilized to provide quantitative analysis of carbon species in the crystalline and amorphous silicates. Furthermore, the combination of multi-nuclear (^{29}Si , ^{27}Al , ^{17}O , and ^{13}C) solid-state NMR and high-pressure synthesis study could provide a powerful tool for understanding the atomistic origins of the speciation of carbon in silicate melts at high pressure, which is essential for understanding the deep carbon cycle and volcanic processes. The current results of carbon speciation in the silicate melts above 4 GPa provide an improved link among the atomic configurations around carbon species, their solubility, the extent of structural disorder, and isotope composition of carbon-bearing melts in the upper mantle.



Evidence for mantle hydration by metasomatism beneath siberian craton

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Water can change physical and chemical properties of mantle minerals, or the part of the mantle, for instance, the effect of OH on mineral deformation and its impact on mantle rheology [1]. Kimberlites are one of the most important objects for research because they carry mantle xenoliths to the surface. So that kimberlites are the only direct source of information on the petrology and geochemistry of the deep mantle rocks. We have studied representative collection of the 19 and 25 relatively fresh xenoliths of peridotites and eclogites, respectively. The xenoliths of peridotites are non deformed and deformed garnet

lherzolites, harzburgite and dunite. The studied peridotites contain 45-70% olivine, 10-40% orthopyroxene, 5-25% clinopyroxene and 10-25% garnet. The garnet bearing peridotites have microscopically recognizable deformation textures. The peridotite xenoliths have granular, porphyroclastic, mosaic-porphyroclastic and fluidal textures [2]. Using different degrees of peridotites deformation we identify three types of lherzolites: non-deformed garnet lherzolites, medium-deformed garnet lherzolites and high-deformed garnet lherzolites. The studied eclogites are biminerally and contain 40-70% clinopyroxene (Cpx) and 30-60% garnet (Grt). Cpx and Grt show wide range of compositions. Clinopyroxenes are characterized by Na₂O (1.7- 7.0 mas.%) and Al₂O₃ (1.9-15.3 mas.%) contents and Mg# 73-92. In garnets almandine component varies from 19 to 48%, pyrope component from 21 to 72%, grossular component from 8 to 33%. All eclogites are divided into three groups by classification scheme of [3], based on MgO and Na₂O contents in Cpx. Using calibration coefficients [4] we calculated water content in mineral samples. Water contents in peridotites range from 2 to 95 ppm in olivine, 8-61 ppm in orthopyroxene, 7-71 ppm in clinopyroxene. The water in eclogites is mainly stored in omphacite (4-99 ppm). Garnets do not contain measurable OH in both rock types. Taking into account the volume ratios of mineral phases in the studied xenoliths, the water contents vary over narrow ranges, from <1 to 61 ppm in peridotites and from 2 to 55 ppm in eclogites. It should be noted that the high-deformed peridotites have the highest water content and vice versa, low-deformed and non-deformed ones contain the low water amounts (Fig. 1). We suppose that higher water contents in deformed peridotites associate with water enrichment of kimberlite fluid, which infiltrate through the peridotite vein. Moreover we obtained no correlation between eclogite water concentration and temperature, pressure or composition of the rock. Low amounts of water in eclogites may be related to intensive dehydration during subduction or partial melting of the rock before kimberlite ascent. The former confirm limited water transfer in subducted slab. This work was partially supported by the Ministry of education and science of Russian Federation, project No. 14.B37.21.0457 and RFBR (projects No 15-55-50033; 15-55- 53029; 16-35-00317). References [1] Miller G.H., Rossman G.R., Harlow G.E. (1987). *Physics and Chemistry of Minerals* 14, 461-472. [2] Harte B. (1977). *Journal of Geology* 85, 279-288. [3] Taylor L. A., Neal C. (1989). *The Journal of Geology*, 551. [4] Bell D.R., Rossman G.R., Maldner J., Endisch D., Rauch F. (2003). *Journal of Geophysical Research* 108, 1-9. [5] Brey, G.P., Koehler, T. (1990). *Journal of Petrology* 31. 1353–1378.



Subduction dynamics, mantle and crustal processes at arc volcanoes, investigated by relative CO₂/ST abundances and ³He/⁴He isotope signatures



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We attempt to correlate along-arc and inter-arc variations of CO₂/ST gas ratios with noble gases and CO₂ compositional trends with the aim to provide a light into the complex transfer of fluids through the mantle wedge to the partial melting zone, while estimating the recycling efficiency of major volatile species along subduction trenches. We have reviewed the available CO₂/ST gas data, along with their respective R/Ra and d¹³C from gas discharges and magmatic crystals, on a data set comprising more than 35 arc volcanoes. We followed by investigating the NVZ, from which compositional and flux data, gas samples and rocks will be analyzed. In respect to our global review, the apparent lack of correlation between CO₂/ST gas ratios and noble gases compositional trends may partly reflect the different sampling techniques and conditions. We argue that the high variability in R/Ra (Min=3.60; Max=9.77) that results may affect our ability to better estimate the extent of such relation. For instance, in Ecuador, a mean R/Ra of 3.3 is estimated, far from the homogeneous MORB signature of 8 ± 1 Ra, highlighting the meaningful data: (i) at a local scale, looking at temporal variations in noble gas composition throughout the course of an eruption, for a particular volcano (e.g., El Reventador, from 2002 to present); (ii) estimating the subduction zone signature of individual arcs and looking at different subduction parameters possibly governing ratio's variability (e.g. different subduction angle and thermal regime within the NVZ); and (iii) improving our ability to use volatile and noble gas trends as geochemical and isotopic precursors of volcanic eruptions.

**Effects of organic matter quality on microbial communities in marine sediments**

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Despite tremendous advances in the study of microbial biogeography in subsurface marine sediments, little is known about the factors determining community structure or the metabolism of the majority of subsurface microbes. In particular, the relationship between organic matter (OM) composition and microbial community structure is poorly understood. Since OM can differ considerably in terms of chemical composition depending on age, source and sedimentary settings, we hypothesize that the macromolecular composition of buried OM is a key factor shaping seafloor microbial communities. To address our hypothesis, we characterized microbial community composition on a transect spanning from the continental shelf to the abyssal plain across one of the most productive marine ecosystems on Earth, the Benguela Upwelling System. Preliminary results show vertical and lateral zonation of communities: within the first meter typical surface sediment groups (Proteobacteria, Thaumarchaeota) progressively decrease and are replaced by characteristic subsurface taxa (Atribacteria, Chloroflexi, Bathyarchaeota and Lokiarchaeota). Coastal non-bioturbated sites show dominance of Thermoplasmata and absence of Thaumarchaeota, opposite of what is observed approaching the abyssal plain. To further elucidate how microbial metabolic potential is changing across the continental margin we analyzed – supported by CoDL - the metagenomes of three subsurface samples representative of different sedimentary settings: inner shelf, depositional center and continental rise. Parallel to the microbial community and metagenome analyses, detailed characterization of the OM present in the transect will be performed. Predominant macromolecular building blocks of the OM will be determined by GC-pyrolysis. The diagenetic status of the OM will be inferred using amino-acid nitrogen to total nitrogen ratios and amino-acid composition-based indicators. Biomarker analysis (GDGTs, alkenones, alcohols) will elucidate the origins of the OM. This extensive organic geochemical dataset will be related to the genetic information through multivariate statistical analysis to test whether certain phylogenetic groups are associated with specific OM fingerprints.

**Using RNA-Seq to understand the metabolically active microorganisms in the deep biosphere**

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Omics analyses (metagenomics, metatranscriptomics, metaproteomics, single-cell genomics, metabolomics, etc.) are being applied on samples from the deep biosphere. The goals are to unveil the taxonomic and functional diversities; and thereby to reveal the role of different organisms in biogeochemistry cycling, the biogeography of taxa and functional groups, and microbial interactions. Many of the bioinformatics tools were initially developed for eukaryotes, especially transcriptomic assemblers for RNA-Sequencing data. This talk will focus on how we approach Illumina reads from total RNA to understand the metabolically active microorganisms found at 1.3 km below the land surface in Beatrix gold mine, South Africa. Five transcriptomic assemblers were evaluated for their performances in revealing the taxonomic and functional profiles. The resultant assemblies varied in quality. The best assemblies, generated by Trans-ABYSS and Trinity, were used to inform the taxonomic composition and metabolic network, respectively. At this depth, in the absence of sunlight and little photosynthetic organic compounds, chemoautotrophs that acquires chemical energy from reduced sulfur and nitrate were predominant. Microorganisms form syntrophic pairs that recycle metabolites so as to overcome the thermodynamic challenges. Methane-oxidizing microbial communities changed over time.

**Growing the 'fast' slowly: Proteomic and Isotopic Phenotyps of sulfate reducers under differential bioenergetic regimes**

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A significant range in microbial lipid 2H/1H ratios is observed in modern marine sediments. The magnitude of hydrogen isotope fractionation between microbial lipids and growth water ($2\epsilon_{\text{lipid-H}_2\text{O}}$) is

hypothesized to relate to the central carbon and energy metabolism. These observations have raised the intriguing possibility for culture independent identification of the dominant metabolic pathways operating in environments critical to the geological record. One such metabolism we would like to track for its global significance in sedimentary carbon cycling is bacterial sulfate reduction (BSR). To-date, BSR are known to produce lipids depleted in fatty acid H-isotope composition, relative to growth water ($2\epsilon_{\text{lipid-H}_2\text{O}} \sim -100$ to -350 ‰), with experiments on different substrates show large-scale variability, but no clear trend. Similarly, aerobic heterotrophs show a wide range in fractionations ($2\epsilon_{\text{lipid-H}_2\text{O}} \sim +300$ to -125 ‰), though a driving mechanism remains unclear. Recent work in aerobic methylotrophs implicates transhydrogenase (TH) exerts a critical control on $2\epsilon_{\text{lipid-H}_2\text{O}}$. This work suggests a specific driving mechanism for this range in fractionation is the ratio of intracellular [NADPH/NADH]:[NADP/NAD], and more fundamentally cellular redox state. In anaerobic bacteria (BSRs, fermenters, others) a key component of energy metabolism is the activity of electron-bifurcating THs, for which a mutant libraries exist in model organisms *Desulfovibrio alaskensis* strain G20 (G20) and the thermophilic fermenter, *Thermoanaerobacterium saccharolyticum* (Tsac). In this study we compare growth rates, fatty acid concentrations and $2\epsilon_{\text{lipid-H}_2\text{O}}$ from wild type and TH mutants in strains of G20 and Tsac. We observed significant growth rate and isotopic phenotypes when TH is involved in energy metabolism (changes in $2\epsilon_{\text{lipid-H}_2\text{O}}$ of >150 ‰ in G20, >30 ‰ in Tsac). We discuss implications for understanding H-isotope fractionation during fatty acid biosynthesis in anaerobic microbes and the potential for interpreting environmental biomarkers records.



Microbial controls on biogeochemical carbon cycling in marine sediments

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Sedimentary environments cover almost $\sim 75\%$ of the Earth's surface and are one of the largest global reservoirs of organic carbon. A major question in carbon biogeochemistry is determining what controls the accessibility or availability of natural organic matter to microorganisms. It is not clear whether microorganisms themselves are ultimately controlling the degradation rate or whether it depends primarily on chemical and physical properties of the compounds. However, understanding the interplay between the organic matter accessibility (or reactivity) and microbial activity is a major challenge due to the inherent complexity and high diversity of both natural organic carbon and microbial communities. In order to overcome many of these empirical challenges, I have developed and validated a novel bioreactor system (IsoCaRB; Beaupre, Mahmoudi & Pearson, 2016) that allows us to continuously monitor and collect respiratory CO_2 quantitatively for natural-abundance isotopic ($\delta^{13}\text{C}$, $\Delta^{14}\text{C}$) analyses. These sequential isotopic measurements provide information on the age and source of natural organic matter being utilized, as well as its rate of remineralization. I have coupled these isotopic measurements with molecular and microbiological analysis to explore the relationships between the reactivity of mixed carbon substrates and microbial activity. Incubations of organic-rich sediment in the IsoCaRB system show how microbial communities respond to a heterogeneous supply of carbon compounds. These results reveal a sequential, selective uptake of different carbon pools illustrating that degradation occurs in a step-wise manner. Changes in microbial community composition, diversity and enzyme activity track the changing nature of the bioavailable substrate (Mahmoudi et al., 2017). This work provides insight into the nature and availability of natural organic carbon which is imperative for elucidating the mechanisms controlling geochemical gradients and the corresponding microbial activities in sedimentary ecosystems.



Magnesite stability in the reduced mantle conditions

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Carbon storage and flux in the deep Earth strongly depends on the oxidation state of the mantle rocks, controlled by oxidation state of iron in minerals and melts. The high amount of FeO presented in the lower mantle [1] and core-mantle boundary will lead to the reduction of carbonates subducted from Earth's surface [2]. MgCO_3 -FeO interaction, a simplified model for the redox reaction between FeO-containing reduced mantle rocks and carbonate-bearing subducted slab was investigated at high pressure conditions (65-130 GP) in a diamond anvil cell. MgCO_3 crystals and Fe foil (99,9%) were used as the starting

materials. The starting materials were loaded in a drilled rhenium gasket. «Sandwich» configuration, where Fe foil was placed between two single-crystal carbonates was used. Two experimental runs were carried out. Pressure was first raised gradually up to the desired conditions at room temperature. Heating was achieved using the double-sided laser-heating technique. Every sample contains two heated areas, obtained at different pressure, with approximate size $\geq 15 \mu\text{m}$. Sample was heated up to 1500-2500 K and annealed during 10-15 min. After quench, pressure was increased, and all procedure was repeated at different spot. Samples were heated at 65-70 GPa, 85-90GPa, and 110-115GPa, 130 GPa. Experiments were conducted in situ using X-ray diffraction to observe phase transformations. X-ray diffraction spectra were measured using a focused monochromatic beam (0.31 Å). The data were processed using following software: Dioptas [3], Fityk [4], and UnitCellWin [5]. Phases were identified using JCPDS databases and previously reported equation of states for individual compounds. Pressure was determined from the calculated unit cell volumes of Fe-hcp using the equation of state proposed by Dewaele et al.[6] Analyses of experimental data showed complexity of the system under investigation caused by phase transformations in the structures of the presented compounds. Formation of wustite (FeO), ferropericlase ((Mg,Fe)O), carbide (Fe₇C₃) and diamond was observed. Magnesite transformation to monoclinic polymorph was observed at about 70 GPa and 1500-2200K. However, formation of high pressure carbonate was not effect sufficiently reaction path, and same products were observed at the pressure range of 65-130GPa. Mg-carbonate reduction can be schematically presented by following reaction:



As the most processes in the mantle, the reaction rate at slab-mantle interface is highly influenced by diffusivity in silicates, which is extremely slow, so that even over the entire history of the Earth only small amount of carbonates can actually decompose by reaction in the lower mantle. In the same time, if carbonates could be transported to the core-mantle boundary, where concentration of iron is significantly higher, they would be completely reduced



Carbon dioxide migration pathways in the volcanic-hydrothermal system of Taal Volcano (Philippines)

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Carbon dioxide flux measurements using an accumulation chamber have been performed up to four times per year since 2008 to monitor degassing of the warm (T=30°C) and acidic (pH = 3.1) Main Crater Lake (MCL) of the active Taal Volcano. Large variations have been seen of up to one order of magnitude. The measured carbon seems to be transported primarily in dissolved form, considering how sublacustrine fumarole maps made after regular sonar surveys between 2011 and 2015 show only minor variation compared to CO₂ flux. Dissolved carbon dioxide (p CO₂) in the lake waters was measured in situ by an infrared gas analyser protected by a PTFE membrane. Spot measurements indicate that p CO₂ is very homogeneous over the entire lake, except for a positive anomaly in the northeast sector of the lake where hydrothermal water enters the lake via sublacustrine springs. A permanent monitoring station was installed in 2013, continuously measuring dissolved carbon dioxide. The high correlation between p CO₂ and CO₂ flux confirms that most of the carbon dioxide is transported to the lake in a dissolved state. An empirical relationship between both parameters was established, and allows us to calculate CO₂ flux hourly, dramatically increasing the temporal resolution of this key volcano monitoring parameter. This new resolution enables us to not only study the effects of volcanic activity, but also meteorological and limnological effects on carbon dioxide migration.



Relationships between Microbial Activities and Subduction-related Outgassing and Volatile Flux at Aleutian Arc Volcanoes

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Subduction-related processes, including the movement and alteration of carbon compounds, are an important component of global geochemical cycles. Actively degassing systems associated with convergent plate volcanism offer interesting opportunities to not only characterize the composition and abundance of volatiles, but also to identify the origin of the discharged gases (e.g. mantle, organic matter, or carbonates). In taking this approach a step further, we have hypothesized that microbial activities in and around fumaroles are influenced by the reduced volcanic gas fluxes. Also, it is conceivable that the source of outgassed volatiles are preferentially consumed by the resident microbes. Therefore, we have designed microbiological studies to investigate the relationships between the volatile gas composition emitted from fumaroles, the microbial activity supported at the surface, and the deep carbon source being subducted. Using a suite of well characterized, coupled fumarole sediments and gas samples, DNA and RNA extractions are being used to describe the microbial community composition using 16S rDNA-metagenomics and transcriptomics, respectively. This “omics” data will be compared to the in situ gas samples collected, allowing for the inference of correlations between the microbiological and geochemical/geophysical characteristics of the sites. Ongoing microcosm studies are aimed at investigating the relationships between the identity of the deep carbon source being subducted, the volatiles being released, and the microbial activities supported at the surface. With this information, we expect to quantify the microbiological input to the global carbon cycle.

**Mineral carbonation in interfacial water films: Influence of nanoconfinement and organic ligands**

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It is critical to understand how the nanoconfinement of aqueous fluids impacts a broad range of natural and industrial processes. Geological examples of nanoconfined environments in the subsurface and soils include interfacial water films, pores, fractures, fluid inclusions, and mineral interlayers. Critical biological processes in cells, proteins, and membranes take place in nanoconfined water, and adsorbed water films on minerals has been identified as possible assembly sites for prebiotic molecules. Additionally, energy materials, engineered barriers, hydrocarbon reservoirs, drug delivery systems, and building materials host nanoconfined water. Due to the widespread importance of understanding reactions in nanoconfined fluids, we have experimentally investigated Mg-silicate carbonation kinetics under interfacial water films of varying thickness (~1.8-2.4 nm) at 35-90 °C. This in situ X-ray diffraction study demonstrated that decreasing water film thickness by a few monolayers of water more than doubled the apparent activation energy for carbonation, from ~34 to ~83 kJ/mol. Additionally, the inclusion of simple organic ligands in the experiments influenced the type and extent of carbonation. The mechanism responsible for these results will be clarified and the CO₂-carbonate-organic ligand interactions in confined subsurface environments will be discussed in the context of the global carbon cycle.

**Using genome sequencing to understand the metabolic capabilities of deep life**

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The terrestrial deep subsurface is a huge repository of microbial biomass, but in relation to its size and physical heterogeneity, few sites have been investigated in detail. I have applied culture-independent genome sequencing to characterize the microbial community composition in deep (up to 3,100 meters below surface) terrestrial fluids at 4 locations spanning two continents. I have reconstructed over 100 genomes from metagenomes (GFMs), enabling the identification of common metabolic pathways. Sulfate- and nitrate/nitrite-reduction were the most common putative energy metabolisms. Complete pathways for autotrophic carbon fixation were found in more than half of the genomes, with the reductive acetyl CoA pathway by far the most common. Whole genome analysis, especially when paired with thermodynamic modeling, or 'Deep Energy' modeling, can be an effective way to understand life and cycling Earth's deep biosphere.

 **The effect of carbon on the formation of volatile-bearing melts at the base of the Earth's upper mantle**

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Volatiles such as H₂O and CO₂ lower the melting temperature of mantle peridotite allowing low-degree partial melts to form in the deep upper mantle, which affect the chemical differentiation of the planet and global geodynamics. Melts forming at the base of the upper mantle has been proposed in fact to cause the depletion of incompatible elements of material upwelling into the shallower upper mantle, as well as causing detectable seismic anomalies. Quantitative constrains on the formation of hydrous melts can be done by investigating the partitioning of H₂O between peridotite minerals and low degree melts (D H₂O min/melt) in the upper mantle. However, experimental studies in hydrous systems suggest that the upper mantle is likely not wet enough to produce melts in its deepest regions, but a more precise description of volatile-induce melting needs to consider the influence of CO₂ as well. We explored the effect of CO₂ on D H₂O min/melt at conditions encountered at the base of the upper mantle (13 GPa and 1400-1800 C) performing high pressure-temperature experiments in a multianvil press. We investigated two sets of starting compositions in the MgO-SiO₂- H₂O - CO₂ system, with similar Mg/Si atomic ratios and different H₂O and CO₂ contents. The H₂O content of upper mantle nominally anhydrous minerals forsterite and enstatite was accurately determined by NanoSIMS (nano secondary ion mass spectrometry) and ERDA (elastic recoil detection analyses) while melt volatile contents were constrained from liquidus phase relations. We observe that modest amounts of CO₂ significantly affect the D H₂O min/melt, enhancing the production of volatile-bearing melts at the base of the upper mantle.

**Metabolic ecology of chemosynthetic nitrate reducing Bacteria from deep-sea vents**

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Metabolism, the biological processing of energy and matter, is driven by multiple redox reactions under extreme physicochemical conditions in deep-sea vents. Chemosynthetic NO³⁻ reduction is a type of metabolism that is emerging as widespread in ε-Proteobacteria and Aquificae, two abundant phylogenetic groups of vent bacteria. Here, we incorporated isotope and aqueous geochemical methods with microbial culturing of ε-Proteobacteria and Aquificae to explore the trade-offs between rates of NO³⁻ respiration (during catabolism) and rates of cell biomass production (during anabolism). We established that metabolic rate-yield trade-offs and ¹⁵N/¹⁴N fractionation signatures associated with NO³⁻ respiration are conserved in cultured vent ε-Proteobacteria and Aquificae in relation to their physiologies. We hypothesize that the population shift from ε-Proteobacteria to Aquificae at deep-sea vents coincides with a shift toward higher rate-to-yield ratio in NO³⁻ respiration at higher temperatures. Further culturing efforts at seafloor pressures suggest that δ¹⁵N discrimination factors for NO³⁻ are independent of pressure effects, while growth yields and NO³⁻ respiration rates are significantly affected by pressure in vitro. Currently, we are complementing our in vitro data with studies using natural vent fluids to further constrain NO³⁻ respiration in situ. Our results provide insights on the ecological assembly rules driving chemosynthetic NO³⁻ reduction activities and their effect on the N biogeochemistry at deep-sea vents.

**Chemical and Physical Aspects of Fluid Extraction within the Earth's Crust**

Mattia Pistone, Georg Zellmer, *University of Lausanne, Switzerland*

The dynamics and kinetics of fluid extraction from lithospheric rocks are essential to the construction of the crust, feeding volcanic eruptions, as well as maintaining a hydrosphere and atmosphere on Earth. In my research, I focus on investigating the chemical and physical properties of multiphase magmas and volatile transport in experimental systems at elevated temperatures and pressures. My main goal is to link the experimental findings with the chemical and physical signatures of natural magmatic systems. Laboratory-based experiments, accompanied by high-spatial resolution analytical investigations, also provide a mean to assess the spatial and temporal dynamics of magmatic and volcanic systems. I will present three scenarios in which fluid extraction processes can be initiated and enhanced by: 1) water diffusion during mafic-felsic magma mixing events; 2) water exsolution in crystallising felsic mushes; 3)

strain localisation in melt- and bubble-enriched portions of multiphase systems. Each mechanism will then be evaluated to determine the efficiency of melt extraction within the longevity of plutonic mushes in the Earth's crust.

Engagement: Filming in the Field

Katie Pratt, University of Rhode Island, USA

Filming in the Field: Scientists often find themselves in unusual locations, places that most people will never be able to visit, from the top of an active volcano to the sleepless halls of a synchrotron. Video is rapidly becoming the most shared form of content online, and is one of the most effective forms of communication. By showing people how and where science is conducted we can better explain DCO research to the world. Sometimes journalists and camera crews do accompany scientists on field expeditions or visit them in the lab, but this is not common. Training scientists to use small, durable, and affordable HD cameras (like the GoPro) allows them to collect high-quality footage wherever they happen to be working. Simple editing programs are also becoming cheaper (if not free), and together with video sharing sites also allow the enthusiastic scientist to create his/her own short films. Topics covered include the importance of video footage to scientific storytelling and DCO outreach, the basic skills required to operate a GoPro camera, and how to storyboard and edit a short film. 5 GoPro cameras and accessories will be available for workshop participants to take on field trips.



Hard rock life - metagenomes from ultradeep terrestrial subsurface

Lotta Purkamo, Malin Bomberg, Claire Cousins, University of St Andrews, UK

We have known the existence of deep biosphere over 20 years, but the microorganisms living in these environments still continue to puzzle us. Microbial life plays crucial role in global carbon cycling and as a significant proportion of Earth's biomass lies in the subsurface, understanding the sources and sinks of C in depths is vital. Only a small fraction of the microorganisms on Earth are cultivable, thus hampering the study of microbial functionality. The development of molecular biological tools has allowed us to progress significantly in understanding the complexity and versatility of deep subsurface communities. The functionality of all life is governed by its genetic code, which we are now able to read due to advances in genome sequencing technology, in particular with metagenomics. We executed metagenomic analyses to microbial communities from ancient deep crystalline bedrock reaching 4.3 km depth, from two different locations in Finland. Primary data based on amplicon sequencing of 16S rRNA gene suggests that the microbial communities in these environments express low diversity. Analysis of metagenomic data retrieved with both state-of-the-art methods as well as emerging nanopore sequencing technology is currently ongoing and the metabolic processes involved in C cycling, stress response, and adaptation to deep life will be identified. Quantitative PCR will reveal the copy number of bacteria and archaea at different depths of bedrock. Furthermore, statistical analyses combining environmental metadata with microbial ecology will be executed. Data retrieved in this study will provide genetic insights into the microbial metabolisms, adaptation and survival in hard rock, and provide constraints on life and habitability.



Challenges to the growth of methanogenic communities in coals seams

Maija Raudsepp, Emma Gagen, Gene Tyson, Suzanne Golding and Gordon Southam, University of Queensland, Australia



Basin-scale studies of coal seam gas composition and the methane $\delta^{13}\text{C}$ and δD stable isotopic values have noted several trends regarding the biotic or abiotic origin of the gas. In particular, there is a trend of decreasing 'biogenic' methane at depth and a relationship between groundwater recharge and periods of 'biogenic' gas production (Golding et al., 2013). However, the exact mechanisms that control this gas distribution are poorly understood. Potential biological factors that could control the activity of methanogenic microbial communities include: 1) the recalcitrant nature of organic carbon in coal 2) nutrient limitations in the deep subsurface (low N and P) 3) the release of inhibitory compounds from coal into the groundwater and/or 4) other physical and chemical factors, such as temperature or salinity.

Based on results from a trickling column bioreactor and batch experiments, we propose that in basins the distribution of biogenic gas may be controlled by the presence of toxic and inhibitory compounds released from the coal. The concentration of these compounds in the groundwater likely depends on the water to coal ratio and the contact time of the groundwater with the coal seam. In addition, the slow rate of methane production is also likely due to recalcitrant and complex composition of coal, which limits energy available for growth.

Golding SD, Boreham CJ, Esterle JS (2013) Stable isotope geochemistry of coal bed and shale gas and related production waters: A review. *International Journal of Coal Geology*, 120, 24-40.



Digging deeper: Is the subsurface really alive?

Brandi Kiel Reese, Laura Zinke, Jordan Bird, Ian P.G. Marshall, Bo Barker Jorgensen, Karen G. Lloyd, Jan P. Amend, *Texas A&M University, USA*

The Baltic Sea is shallow intracontinental sea that receives marine input from the North Sea and riverine input from Scandinavia and continental Europe. This input contributes to high sedimentation rates in the basin, which results in organic rich anoxic sediments. In 2013, the Integrated Ocean Drilling Project Expedition 347 collected deeply buried sediment from the Baltic Sea Basin for paleoclimatological and microbiological research. Here we present analyses of the active resident microbial communities from three samples. We used metatranscriptomic sequencing of in situ RNA and determined that Chloroflexi and Atribacteria are the dominant active populations in our samples. Functional analysis expressed genes demonstrate that fermentation is a key metabolic process in these sediments. Cycling of carbon, nitrogen, phosphorus is mediated through mainly assimilatory and degradative processes. Genes for cell division are also expressed, indicating that a portion of the in situ microbial community is actively dividing. This study supports the argument that microbes in the deep biosphere are alive, active, and biogeochemically relevant.



Microbial dumpster diving: Deep-sea heterotrophs that specialize on the degradation of dead biomass

S. Emil Ruff and Gunter Wegener, *University of Calgary, Canada*

In the recent past we have gained substantial insights into the diversity and ecophysiology of autotrophic organisms inhabiting cold seeps and hydrothermal vents. Yet, little is known about the heterotrophs that thrive in these ecosystems, and their role in the carbon cycle. Since organic carbon input into the deep-sea is extremely low, the heterotrophic organisms must use the autochthonous organic carbon that was fixed by the autotrophs, thereby passing deep subsurface derived energy and carbon up the food chain. We thus hypothesize that seeps and vents harbor heterotrophs that are specialized on the degradation of dead microbial biomass and cell components. To address this question we used a multi-dimensional enrichment strategy, providing different temperatures, carbon sources and electron acceptors to microbes that originated from hydrothermal sediments of Guaymas Basin. First results show that, indeed, we enriched communities that specialize on the degradation of specific cellular components such as proteins, nucleic acids, lipids, or polysaccharides. Metagenomic and metaproteomic data are currently being produced and will likely reveal the involved populations and pathways. Our research addresses an important gap in the understanding of cold seeps and hydrothermal vents, which are windows to the deep biosphere. Hence, the expected insights have implications not only for surface ecosystems, but also for the deep subsurface.



Linking Large Igneous Province volcanism to the initiation of a major negative feedback mechanism in the global carbon cycle



Micha Ruhl, Weimu Xu, Stephen Hesselbo, Hugh Jenkyns, Jim Riding, Marisa Storm, *University of Oxford, UK*



Earth history is marked by major volcanic events, sometimes associated with the emplacement of a large igneous province (LIP). The release of greenhouse gasses and toxic compounds at such times had a major impact on global biogeochemical cycles, climate, the environment and the biosphere. Carbon

release from LIPs typically occurred over 100–1000s of kyrs. The magnitude of associated global carbon cycle perturbations, typically recorded as positive or negative perturbations in continental and marine carbon-isotope records, are controlled by the initiation of positive and negative feedback mechanisms in the Earth system. Here, we present an Early Jurassic (~180 Ma) case-study, in which major Karoo-Ferrar LIP emplacement and associated carbon release initiates a previously unconstrained negative feedback mechanism in the global carbon-cycle. Carbon release and associated climatic change at that time cause the formation of major inland lakes that draw down carbon from the ocean-atmosphere system and thus shorten the global carbon cycle perturbation by 10–100s of kyrs.



Geomicrobiology of extreme environments

Cody Sheik, University of Minnesota Duluth, USA

Microorganisms are extraordinary catalysts that arose early in Earth's geologic history and have since evolved cellular machinery that contribute to most of Earth's low-temperature geochemical cycles. My laboratory takes a multi-disciplinary approach that combines microbial ecology, physiology, genomics and geochemistry to address fundamental microbial systems questions that scale from a single microbial cell to the entire ecosystem. To address our questions, many of which are first order due to the state of the field, my lab combines traditional microbiology techniques of isolation and enrichments with molecular based approaches (such as metagenomics and metatranscriptomics), and geochemical approaches to elucidate the function and contribution of microorganisms in the environment. To date, the lab has sampled from several extreme systems — such as fumaroles and hydrothermal vents — but are currently focused on two systems; deep, oligotrophic, freshwater lakes (sediments and water column) and glacial systems. In these systems, my lab is concentrating on understanding how carbon flows through microbial communities and is potentially coupled to other potentially cryptic, biogeochemical cycles.



Geochemical and experimental evidences of a gradual increase of the mantle redox state before and during the Archean: implications for the habitability of Early Earth



Vincenzo Stagno, Steeve Greaux, Yoko Kebukawa, and Tetsuo Irifune, Sapienza University of Rome, Italy

The composition of the Earth's early atmosphere can be thought as the result of 1) significant release of volatiles that occurred as consequence of the Hadean Late Heavy Bombardment (LHB), 2) the oxidation state of Archean outgassing magmas and 3) the inherited volatile budget of the accreting chondritic material. It is commonly thought that the oxygen fugacity (f_{O_2}) of the Earth's mantle has remained constant within -1 and 0 log units (normalized to fayalite-magnetite-quartz buffer, FMQ) in the last 4 Ga. This would imply that the composition of the atmosphere during the Archean was similar to today suggesting that the Earth became habitable in very short time after his accretion [1,2]. However, the V/Sc ratio of preserved Archean orogenic and mantle eclogites that have low-pressure protoliths unravel the redox history of the convecting mantle. Archean convecting mantle is shown to have been more reducing than its modern equivalent, as previously suggested, with ΔFMQ as low as -1.5. This has several consequences such as, (1) the locus of a volatile-bearing peridotite solidus and the composition of fluids/melts that formed along the mantle adiabat; (2) redox melting as a precursor to continental rifting during which carbonatitic to carbonate-silicate melts might have been the first magmas to be erupted, and (3) the increase in atmospheric CO_2 accompanied by first whiffs of oxygen. The possible effects of the LHB on the gradual increase of the mantle f_{O_2} and, in turn, the preservation of habitable early environments has been highly debated. We will discuss preliminary results from experiments performed at high pressure and temperature using natural volatile-rich carbonaceous chondrite, Tagish Lake (C2), to investigate the volatile speciation during petrologic processes and their influence to the survivability of thermophile organisms during asteroid impacts [3]. [1] Li and Lee (2004) EPSL 228, 483-493. [2] Scaillet and Gaillard (2011) Nature 480, 48-49. [3] Sleep NH (2010) Cold Spring Harb Perspect Biol; 2:a002527.

**Experimental viscosity measurements of carbonatitic magmas at pressures and temperatures of the Earth's upper mantle**

Veronica Stoppioni, Vincenzo Stagno, Yoshio Kono, *Sapienza University of Rome, Italy*



Carbonatites are igneous rocks either intrusive or extrusive that crystallize during cooling of a magma (or lava) with more than 50 wt% of a carbonate component and less than 10 wt% of silica (SiO₂), likely originated by partial melting of mantle rocks in presence of CO₂ other than shallower processes such as liquid immiscibility and fractional crystallization of magmas during their ascent up to the surface. Although many studies have been carried out over the last decades in order to understand the origin of carbonatitic magmas at depth, their rheological properties, such as density and viscosity, result little known yet. The main aim of this study is to determine experimentally the viscosity of carbonatitic magmas at pressures and temperatures of the Earth's upper mantle, to calculate their ascent velocity from the source rock to the Earth's surface. Experiments were conducted at pressures of 1.5-6 GPa and temperatures between 1050 and 1500 °C where the "falling sphere" technique was used to determine the viscosity of synthetic carbonatitic melts. The target pressures were achieved using the Paris-Edinburgh press combined with in situ X-ray diffraction at Advanced Photon Source (Argonne, USA). Here, the use of synchrotron radiation allowed to collect a series of radiographic images (500-1000 frames per second) necessary to monitor the falling sphere as function of time and, in turn, determine the viscosity using the Stokes' equation including the correction factors for the effect of the wall and the end effect. The recovered quenched products were analyzed with the scanning electron microscope and the electron microprobe to investigate their texture and chemical composition. The experimental results obtained represent the first preliminary data that can be used in the field of geodynamic modeling of the ascent of primary carbonatitic magmas and carbon speciation from the mantle up to the surface as function of time.

**Real-time gas monitoring of a fumarolic field: application at La Soufrière of Guadeloupe (Lesser Antilles)**

Giancarlo Tamburello, Vincent Robert, Jean-Christophe Komorowski, Thierry Kitou, Patrick Allard, Arnaud Lemarchand, Celine Dessert, Anne Le Friant, Marc Chaussidon, *INGV Bologna, Italy*

Fumarolic fields of closed-conduit volcanoes are often characterized by heterogeneous chemical compositions in response to varying hydrothermal/magmatic inputs. Monitoring in real-time how this contribution varies spatially and temporally may contribute to evaluate improve the understanding and assessment of future volcanic unrest. Here we report on the first deployment of a MultiGAS network for measuring the CO₂- H₂S - SO₂ gas molar fractions in the major fumaroles of the La Soufrière volcano of Guadeloupe island (Lesser Antilles) which is characterized by the intensification of decadal fumarolic emissions after the 1976-1977 non-magmatic eruptive crisis. Data from this continuous telemetered MultiGAS network will be complementary to in-situ fumarole gas sampling performed by the OVSG since 1979 and to periodic MultiGAS surveys through the gas plume. High-frequency gas surveys at La Soufrière will provide key insights into pre- and syn-eruptive volcanic processes, will help refine/implement models of the dynamics of the magmatic/hydrothermal system, as well as provide better constraints on the source mechanisms controlling degassing, thermal and seismic energy release in the context of moderate yet persistent and evolving unrest since 1992.

**Formation Fe³⁺-rich majoritic garnets and diamond from redox reaction between recycled carbonate and mantle rock**

Renbiao Tao, *Carnegie Institution for Science, USA*

Majoritic garnet [(Ca, Mg, Fe²⁺)₃(Fe³⁺, Al, Si)₂(SiO₄)₃] is one of the predominant and important constituents of upper mantle peridotite and ultra-deep subducted slabs. The charge balance calculations show that majoritic garnets from mantle diamonds could contain significant Fe³⁺ contents (Fe³⁺/Σ Fe up to 0.95). We recently reported some Fe³⁺-rich majoritic garnets inclusions (Fe³⁺/Σ Fe > ~ 0.81) from the deep upper mantle (> 380 km), which was brought to Earth's surface by carbonatite (Xu et al., 2017). These observations motivated us to investigate the role of Fe³⁺ in the majoritic garnet structure and formation mechanism of Fe³⁺-rich majoritic garnet in deep upper mantle. We systematically synthesized

Fe³⁺-bearing majoritic garnets from 6.5 GPa to 15 GPa and evaluated the effect of Fe³⁺ on the majorite geobarometer. The Fe³⁺ contents of synthetic majoritic garnet were analyzed using the “Flank method” with the electron probe microanalyzer (EPMA). Our results show that the existing majorite geobarometer, which does not take into account the Fe³⁺ substitution, could underestimate the formation pressure of majoritic garnets, especially for samples with a high majoritic component. Further high-pressure experiments in the system of carbonate and Fe²⁺-mantle rock shows the redox reaction between recycled carbonate and mantle rock could be the formation mechanism of Fe³⁺-bearing majoritic garnet and diamond/graphite.



Parameterizing devolatilization of subducted lithologies and modelling deep carbon transport during subduction process

Meng Tian, Richard F Katz, Dave A May, *University of Oxford, UK*



The subduction of carbonate-bearing rocks into Earth’s mantle and its return to the surface are linked by metamorphic degassing and arc volcanism. A grand question exists as to whether the CO₂ released in the deep can balance that degassing on the surface in subduction-zone settings. Earlier thermodynamic studies of decarbonation suggest that at sub-arc depths, only a small fraction of CO₂ is released from the slab, insufficient to balance the arc volcanic CO₂ release if the fluid flow directions within mantle wedge is upward (Kerrick and Connolly, 1998, 2001; Gorman et al., 2006). Furthermore, compilation of field-derived CO₂ fluxes suggests that all the carbon in the downgoing slab is stripped off and migrates to shallow depths and atmosphere, implying that subduction cannot bring carbon into the deeper mantle in the long run (Kelemen and Manning, 2015). Nonetheless, due to field sampling biases and the uncertainties of fluid flow directions within both the slab and mantle wedge (Wilson et al., 2014), the question above is still open for numerical studies. In my general science talk, I plan to expose the above question to both petrologists and modelers. In my technical poster, I will present the efforts we have made to parameterize the devolatilization (CO₂ and H₂O) of subducting lithologies--metasediments, metabasalts, metagabbros, and how this parameterization interfaces with the two-phase flow modelling in subduction zones to quantitatively map carbon transport there.



Direct dating of microbial methane oxidation in deep crustal fracture systems

Mikael Tillberg, Henrik Drake, Thomas Zack, K. Johan Hogmalm, Nick M. W. Roberts, Mats E. Åström, *Linnaeus University, Sweden*



Minerals precipitated in fault and fracture systems in crystalline bedrock disclose information about tectonothermal events, palaeohydrological conditions, ancient microbial activity and other bio- and geochemical processes in the deep subsurface. Recent mineralogical and isotopic studies have revealed extensive signs of deep ancient life in the deep continental crust (e.g. microbial methanogenesis, sulphate reduction and methane oxidation). However, temporal constraints of these ancient microbial activities remain elusive due to the minor amounts (or complete absence) and fine-grained and/or zoned nature of bio-related minerals suitable for direct dating by radiogenic isotope analysis. With the advent of newly developed in situ Rb-Sr dating methodology by reaction cell LA-ICP-MS/MS as well as U-Pb LA-ICP-MS dating of carbonates, absolute geochronological data with detailed spatial (50 µm) resolution and high analytical precision is now accessible. These techniques are applied to polished mineral and rock sections following detailed petrological characterization to target sample areas suitable for analysis and to ensure that Rb-rich and Sr-rich phases formed and remained in equilibrium to constitute a valid isochron. By textural localization and in situ isotopic analysis of discrete crystal growth zones, multiple fault reactivation pulses and periods of extensive microbial activity are unveiled in deep drill core samples from 1.87-1.80 Ga old granitic bedrock at Laxemar and Forsmark areas, SE Sweden. Several low-temperature Palaeozoic precipitation events are recorded in co-genetic adularia and calcite overgrowths where extensive fluid inclusion and stable isotope composition data constrain the prevailing geochemical and geothermal conditions at the time and site of precipitation. δ¹³C signatures in authigenic calcite reveal the spatially and temporally dynamic nature of a carbon cycle mainly related to methane circulation in the deep fracture systems. Large variations and extreme values of δ¹³C in calcite evidence ancient episodes

of methanogenesis and anaerobic oxidation of methane (AOM) in the upper 800 m of the crystalline basement in the studied areas. The exceptionally light $\delta^{13}\text{C}$ signatures of calcite and the $\delta^{34}\text{S}$ values of co-genetic pyrite suggest that AOM proceeds by a microbial consortium consisting of anaerobic methanotroph archaea and sulphate-reducing bacteria. The connected AOM and bacterial sulphate reduction occurs where methane mixes with saline sulphate-rich water, which in one of the areas is at great depth, thereby representing a sulphate-methane transition zone that is reverse to what occurs in sedimentary settings. In situ Rb-Sr dating of fossil biofilm (now almost completely fossilized to K-rich clay minerals) in combination with organic $\delta^{13}\text{C}$ values of co-genetic calcite and preserved organic compounds of surficial origin (e.g. land plants) determines the minimum age of the microbial life. The deep methane oxidation is traced back to the Devonian period. In summary, the geochronological results temporally constrain fault and fracture reactivation that enabled microbially mediated methane production and consumption in the deep terrestrial crust, consequently yielding insights into the fluid migration incidence that may have had significant control on subsurface carbon cycling over geological eras. This multi-disciplinary study thus connects the deep biosphere, geochemistry of fluid-rock interactions and geochronology of tectonic events by using techniques that can directly date a wide range of common secondary mineral assemblages and other geological features where small sample sizes and amounts inhibit utilization of conventional methods.

**Fermenters shall inherit the Earth: Estimates of deep biosphere activity in 2,000 mbsf coal beds utilizing passive tracer and minimal carbon and nitrogen amended SIP-NanoSIMS incubations**

Elizabeth Trembath-Reichert, Yuki Morono, Akira Ijiri, Tatsuhiko Hoshino, Katherine S. Dawson, Fumio Inagaki, Victoria J. Orphan, *MBL/WHOI, USA*

The past decade of marine scientific drilling has led to the discovery of seemingly ubiquitous microbial life in a range of deep biosphere habitats. In a quest for possible depth limits to deep life, IODP Expedition 337 successfully recovered core down to a record-breaking 2.5 km below seafloor (kmbsf) from a deeply buried coal bed system with low thermal alteration. Shipboard analyses showed coal beds were “hot spots” of microbial life, with cell concentrations 10 to 100 times higher than surrounding lithologies. To estimate potential microbial activity and the ability to utilize methylated compounds derived from coal degradation, 2.5 year-long stable isotope probing (SIP) incubations were carried out at in situ temperatures (37 to 45 °C) with deuterated water (passive tracer) and minimal ^{13}C -carbon and ^{15}N -nitrogen amendments. ^{13}C and 2H isotope incorporation into dissolved inorganic carbon and methane pools was non-destructively monitored during incubation to track activity, with NanoSIMS analysis performed on the most geochemically active incubations. While cells were scarce, ranging from 50 to 2000 cells/cm³ in the most active incubations, we successfully determined potential hydrogen and nitrogen biosynthesis turnover times of less than a year to hundreds of years from single-cell NanoSIMS isotopic incorporation into biomass. These turnover time estimates were orders of magnitude lower than previous deep biosphere studies and demonstrate the power of single-cell analysis in deep biosphere systems. Isotopic and genetic data also support a predominately fermentative microbial community remained active in these incubations, rather than the methanogenic community expected based on on-board geochemistry and more nutrient-rich incubation techniques.

**Serpentinization: Reactive transport processes and hydrothermal fluxes**

Benjamin Tutolo, Nicholas Tosca, Juergen Thieme, *University of Calgary, Canada*



Serpentinization occurs wherever olivine interacts with water at temperatures under ~350°C on Earth and likely on many silicate-bearing extraterrestrial bodies. Serpentinized rocks commonly show evidence of “reaction-driven cracking,” a self-propagating process wherein the dramatic solid volume increases associated with serpentinization continuously generate new flow pathways and reactive surfaces by fracturing the rock. Logically, this process requires that the rate of reaction is faster than the rate of solute transport away from the reacting surface. The porosity and permeability of igneous rocks are inherently low and, hence, reaction-driven fracturing may be intuitively expected to occur wherever the temperatures and pressures are thermodynamically and kinetically favourable. Nonetheless, it is difficult to reconcile the

seafloor expression of serpentinization—high-flux hydrothermal vents—against the low flow rates required by reaction-driven cracking. Here, I present new conceptual models of serpentinization that take into account the particular effects of reactive transport processes on serpentinization-driven hydrothermal fluxes using a combination of recent experimental and field observations, numerical calculations, and estimates of paleo-seawater composition. I will particularly focus on the effects of SiO₂ cycling in both modern and ancient environments and its influence on the partitioning and oxidation of Fe, which, in turn, controls fluxes of life-sustaining H₂.

**Infrasonic resonance of volcanic craters**

Leighton M. Watson, Eric M. Dunham, Jeffrey B. Johnson, *Stanford University, USA*

Volcanic activity frequently generates low frequency acoustic waves, termed infrasound because it is below the audible frequency range. Infrasound observations are used in volcano monitoring and can be used to infer eruption properties such as volume flux, gas exit velocity and plume height. Harmonic infrasound signals, with a pronounced fundamental tone, have been observed at a number of open-vent volcanic systems including Cotopaxi, Erebus, Villarrica, and Kilauea, where outgassing or explosive bubble bursts excite acoustic waves and resonant modes of a crater. Infrasound records contain information about the properties of the volcano, such as the geometry of the crater, spectral content of the acoustic source, and volumetric flux of fluid ejected at the bottom of the crater. We develop a model of the acoustic waves inside the crater in order to extract information about crater geometry and crater floor gas flux. We demonstrate how an understanding of the resonant modes of the crater could be used to forecast eruptions of open vent volcanoes, such as the March 3rd, 2015 eruption of Villarrica volcano, Chile. In addition, we discuss ongoing work developing a computational fluid dynamics model of the volcanic jet. This model will facilitate a more sophisticated description of the acoustic source and account for nonlinearities in the acoustic wave propagation. The goal is to enable infrasound observations to be more accurately inverted for eruption properties such as gas flux.

**Fluid-rich diamonds through time – a new approach to unraveling Earth history**

Yaakov Weiss, LDEO Columbia University, USA

Our understanding of how the Earth operates through plate tectonics is to a large extent due to basic research on processes in the deep Earth. However, while we are able to directly observe the surface responses to deep Earth processes, almost all geochemical or geophysical studies of the deep Earth are indirect. For example, deep Earth characteristics are inferred from magmas, which are not direct samples but rather partial melts, and interior physical properties are inferred from seismic waves. Diamonds, on the other hand are very special in that they offer unique ‘windows’ to look directly at deep parts of the Earth. They form at depths >140 km beneath the Earth’s surface, from circulating hot carbon- and water-rich (C-O-H) fluids, which are often encapsulated as ‘fluid microinclusions’. Due to the physical strength and chemically inert nature of their diamond host, these inclusions remain pristine for billions of years, and represent our only direct samples of deep Earth C-O-H fluids. The few published studies on deep C-O-H fluids conclude they are cycled between the Earth’s surface and interior. Ongoing comprehensive study of the major and trace elements and isotopic composition of C-O-H fluid-rich diamonds from different continents will allow to provide the first radiometric ages of C-O-H fluids in diamonds, and to document their role in the context of global plate tectonics through Earth’s history. The results will have major impact on our understanding of the deep carbon and water cycle, and the role of deep C-O-H fluids in Earth processes and the global circulation of volatiles.



Kristin Woycheese, D’Arcy Meyer-Dombard, Dawn Cardace, Carlo A. Arcilla, Shuhei Ono, *Massachusetts Institute of Technology, USA*

Serpentinization is a metamorphic process that yields serpentine, brucite, and magnetite from the dissolution of olivine. Hydrogen and methane gas are also produced, resulting in ultrabasic (pH > 10), Ca²⁺-rich fluids. In the deep subsurface, these conditions fuel microbial food webs that are decoupled from the products of photosynthesis. Throughout the Solar System, the same process may help craft

habitable environments on rocky bodies such as Mars or Europa. In the Philippines, serpentinizing springs and gas seeps emanate from the Zambales Ophiolite Complex. While the bulk of methane production is assumed to be abiotic, hydrogenotrophic methanogens have been detected in serpentinizing fluid from these springs, and bioenergetic models suggest that methanogenesis may be favorable in such environments. Here we present the first study of methane clumped isotope (^{13}C H3D) signatures from the Philippines to identify any biogenic signature in serpentinization-associated springs and seeps. Using tunable infrared laser direct absorption spectroscopy (TILDAS), we identify the ratio of methane clumped isotopes to constrain the temperature of equilibration in the system. Coupled with metagenomic analysis of microbial communities in serpentinizing fluids and sediments, we evaluate the plausibility of a biogenic component to the clumped isotopic signature of serpentinization-associated methane in the Philippines.

**The role of plate tectonics and mantle convection in the deep-time and deep-Earth carbon cycle**

Sabin Zahirovic, R Dietmar Müller, Jodie Pall, Sebastiano Doss, Madison East, Louis Johansson, Simon Williams, Rakib Hassan, John Cannon, *University of Sydney, Australia*



Plate tectonics and mantle convection drives the exchange of carbon between deep and shallow reservoirs, as well as sustaining the conditions on our planet that are necessary for life. True plate tectonic reconstructions, especially of Pangea supercontinent assembly and breakup, have been underutilized in better understanding the deep carbon cycle until very recently. We use the open-source GPlates plate reconstruction platform from which we extract the geometry of subduction zones, age of the subducting oceanic crust, and plate velocities at 1 million year intervals. This allows us to estimate subducting plate area, which we use to estimate slab flux and the time-varying input of volatiles at trenches. We then investigated the interaction of arc volcanism and carbonate platforms in a deep-time plate tectonic reconstruction framework since the Devonian (410 million years ago). More recently, we have explored the input of CO_2 from Large Igneous Province eruptions, including the subsequent CO_2 sequestration from silicate rock weathering in the equatorial humid belts. We also link our plate reconstructions to global 4D mantle convection modelling, which helps us track the fluxes of plume and slab material. These models provide boundary conditions for our surface process models of basin evolution, including carbonate platform growth in shallow marine environments. These efforts encompass our long-term goals of crossing spatial and temporal scales in numerical models, as well as incorporating interdisciplinary approaches to modelling complex Earth systems using the latest supercomputing technologies.